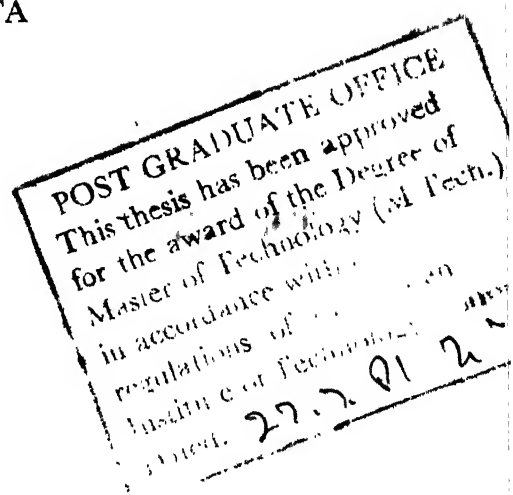


STUDIES ON LINEAR POLYCONDENSATION AND ON NYLON 6 POLYMERIZATION

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
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INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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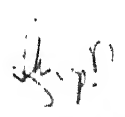
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CERTIFICATE

This is to certify that the work 'Studies on linear polycondensation and on nylon 6 polymerization' was done under my supervision and that it has not been submitted elsewhere before for a degree.


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ABSTRACT

The work consists of two parts. In part 'A' a parametric study has been made on the condensation polymerization of ARB type monomers and on polymerization between monomers of type ARA and AR'B, for the case where the equal reactivity hypothesis is not valid. The analysis has been done for a segregated CSTR. For ARB type monomer the molecular weight distributions and their moments have been compared for two different kinetic models, suggested before. These two models have been extended to the other case and a third model is proposed.

In part 'B' reversible hydrolytic polymerization of ϵ -caprolactam to nylon 6 in a batch reactor has been studied. The primary purpose was to simulate the reactions in the polymerization process and to establish a computationally efficient mathematical technique for solution. The approach was not successful, however, for the system considered here due to a problem of computational instability. Possible reasons for the failure and possible ways to overcome this problem have been discussed.

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NOMENCLATURE

Part A

f_{PO}, f_{QO}	fractions of initial monomers P_1 and Q_1 , respectively in ARA + BR'B
k_I	the first rate constant in the models of unequal reactivity
k_p	the second rate constant in the models of unequal reactivity
M_O	total original concentration of monomers in ARA + BR'B
M_k	dimensionless k-th moment in ARB type condensation polymerization
$\overline{M}_p^{(k)}, \overline{M}_Q^{(k)}, \overline{M}_S^{(k)}$	k-th moments for distributions of species P, Q & S, respectively
P_{10}, Q_{10}, S_{10}	Initial monomer concentrations in ARA + BR'B polymerization.
P_n	bifunctional chains with both end groups A in ARA + BR'B type polymerization
Q_n	bifunctional chains with both end groups B in ARA + BR'B type polymerization
R	ratio k_I/k_p
S_n	bifunctional chains with A & B as the end groups, in either ARB type or ARA + BR'B type polymerization.
X	dimensionless batch time, $k_p P_{10} t$ for ARB, and $k_p M_O t$ for ARA + BR'B

Z_n	dimensionless concentrations in ARB type polymerization
τ	actual reactor - holding time in CSTR
θ	dimensionless reactor holding time in CSTR, $k_p P_{10} \tau$ for ARB and $k_p M_0 \tau$ for ARA+BR'B
μ_N, μ_w	Number average and weight average chain lengths
P	Polydispersity Index

Part B

a_0	initial concentration of acids or amines
A_n	concentration of monofunctional chains of length n
B	constant used in the equation depicting the functionality of cyclization equilibrium constant $K_3(n)$ with n
C_1	monomer concentration
C_n	concentration of macrorings with n repeating units
C_n	coefficients of Laguerre polynomials
$G(x)$	the normalized distribution
G_j	abbreviations for the j -th moment of $G(x)$
$=k$	
G_x	k -th moment of normalized distribution $G(x)$
k_1^0, k_2^0, k_3^0	rate constants for the uncatalyzed reactions in caprolactam polymerization
k_1^c, k_2^c, k_3^c	rate constants for the catalyzed reactions in caprolactam polymerization.

k_1, k_2, k_3	forward reaction rate constants
k'_1, k'_2	reverse rate constants for ring opening and polycondensation, respectively.
$k'_3(n)$	cyclization reaction rate constants as function of ring length n
K_1, K_2	Equilibrium constants for ring opening and polycondensation, respectively
$K_3(n)$	cyclization equilibrium constants, as function of ring length n
$L_n(x)$	generalized Laguerre polynomial of order n
$M(v)$	the continuous distribution used for the actual discrete distribution
$M_v^{(k)}$	k -th moment of distribution $M(v)$
N_{max}	the number of moments used in Min's method
S_1	concentration of amino caproic acid
S_n	concentration of the bifunctional chains of length n
v	the argument in the continuous distribution $M(v)$
W	water concentration during polymerization
x	the argument in the normalized distribution function $G(x)$
$\Gamma(x)$	gamma function of argument ' x '
α	free parameter in the generalized Laguerre polynomials

β_n	n-th moment for monofunctional chains distribution
λ_n	n-th moment for bifunctional chains distribution
γ_n	n-th moment for macroring distribution

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PART A

STUDIES ON UNEQUAL REACTIVITY IN LINEAR POLYCONDENSATION

CHAPTER A-1Introduction:

Usually in the study of the kinetics and the molecular weight distribution of linear condensation polymerizations, the assumption is made that the reactivity of a functional group is independent of the nature and length of the chains to which it is attached⁽¹⁻⁵⁾.

However, many systems have been reported for which this assumption is not valid, e.g. polymerization of alkali metal salts of p-chloro- and p-fluorothiophenols⁽⁶⁾, formation of polyethylene terephthalate^(7,8) and polymerization of diisocyanates^(9,10) and of phenol for maldehyde systems⁽¹¹⁻¹⁴⁾. The violation of the equal reactivity assumption for polymerization between acid anhydrides and aromatic diamines has been reported⁽¹⁵⁾, and it has been shown⁽¹⁶⁾ that the MWD in the condensation product of divinyl benzene with p-cresol is different from that predicted using this hypothesis.

Model studies on this change of reactivity have been relatively fewer. Kronstadt et.al.⁽¹⁶⁾ used two different rate constants in their kinetic scheme with partial success in matching the theoretical prediction with experimental data. Miller and Macosco^(17,18) have considered stepwise polyfunctional

polymerization where functional group reactivities in the same monomer change due to a substitution effect. Ozizmir and Odian have analysed linear step polymerization between AA and BC monomers⁽¹⁹⁾ and between AA,BB and CC type monomers⁽²⁰⁾, where B and C are functional groups of the same nature but having different reactivity. Gandhi and Babu have considered the change in reactivity of functional group due to asymmetry or substitution effect in the molecule⁽²⁴⁾, and due to originally present asymmetry and induced asymmetry on the same molecule⁽²⁵⁾. Kumar, Gupta and coworkers have considered violation of the equal reactivity hypothesis in phenol formaldehyde systems⁽¹³⁻¹⁵⁾ and have proposed two kinetic models on general linear polycondensation of ARB type monomers⁽²¹⁻²³⁾. However, all these are studies on batch reactors.

Condensation polymerizations in CSTR's are important industrially but few researchers have worked on it. Biesenberger⁽²⁶⁾ computed the polydispersity indices in a micromixed model of CSTR. Based on the same hydrodynamic model, Gupta et al.^(27,28) obtained the MWD and its moments for the two proposed kinetic models by them earlier for batch reactors⁽²¹⁻²³⁾.

It should be noted that for the polymerization in a CSTR, a microscopic segregation model is often closer to the actual case than the micromixed model particularly because of

the high viscosity involved. Tadmor and Biesenberger⁽²⁹⁾ found the MWD's and their moments for condensation polymerizations carried out in a segregated CSTR, for ARB type monomer following the equal reactivity hypothesis. In this work we take the two models proposed by Gupta et al⁽²¹⁻²³⁾ and make a theoretical parametric study on the corresponding MWD's and moments in a segregated CSTR. We then extend these models which were originally for ARB type, to ARA + AR'B type polycondensations and also propose a third model to make a closer approximation of some real cases. In both the cases the reaction is assumed to be irreversible which implies that the condensation product is withdrawn as soon as it is produced.

CHAPTER 2-2FORMULATION

ARB type monomer: In such a reaction at any time only one family of molecules will be present, namely, S_n . The general reaction is: $S_m + S_n \xrightarrow{K_{p,mn}} S_{m+n} + \text{condensation product}$. The two models proposed are the two limiting cases of real polymerizations:

Model I

$$\begin{aligned}
 K_{p,11} &= k_{11}/2 \\
 K_{p,mn} &= k_p: m=n, m,n=1,2, \\
 &= k_p/2; m=n, m,n > 1
 \end{aligned} \tag{1}$$

Model II

$$\begin{aligned}
 K_{p,11} &= k_{11}/2 \\
 K_{p,1n} &= k_{11}, \quad n > 1 \\
 K_{p,mn} &= k_p, \quad m \neq n; m,n > 1 \\
 &= k_p/2, \quad m=n, m,n > 1
 \end{aligned} \tag{2}$$

The corresponding rate equations for species and moments, in dimensionless form, for batch reactors, are given in Table A1.

In an SCSTR there is a residence time distribution and in an ideal CSTR, it varies from zero to infinity with a RTD

$$\text{function } E(t) dt = \frac{1}{\tau} \exp(-t/\tau) dt \quad (30)$$

The average outlet concentration of S_n is given by^(29,30)

$$S_n = \frac{1}{\tau} \int_0^{\infty} S_n(t) \exp(-t/\tau) dt \quad (4)$$

To make the equations dimensionless we define $x = k_p S_{10} t$ and

$$Z_n = \frac{S_n}{S_{10}} \quad \text{and} \quad \theta = k_p S_{10} \tau, \quad (5)$$

So the dimensionless outlet concentration from the segregated CSTR is given by

$$\hat{Z}_n = \frac{\hat{S}_n}{S_{10}} = \frac{1}{\theta} \int_0^{\infty} Z_n \exp(-x/\theta) dx, \quad n = 1, 2, \dots \quad (6)$$

From the batch concentrations of S_n one can get the outlet concentration by integrating equation (6). Molecular weight distributions may be calculated by the following equation

$$\text{mass fraction of } n\text{-mer} = \frac{n \hat{S}_n}{\sum n S_n} = n \hat{Z}_n \quad (7)$$

The values of the moments in the outlet of the SCSTR can similarly be obtained by using the equation

$$\hat{M}_k = \frac{1}{\theta} \int_0^{\infty} M_k \exp(-x/\theta) dx; \quad k=0, 1, 2, \dots \quad (8)$$

$$\text{where } M_k = \sum_n n^k S_n / S_{10}, \quad k=0, 1, 2, \dots \quad (9)$$

The molecular weight averages can then be obtained as follows

$$\hat{\mu}_n = \hat{M}_1 / \hat{M}_0, \quad \hat{\mu}_w = \hat{M}_2 / \hat{M}_1, \quad \hat{p} = \hat{\mu}_w / \hat{\mu}_N \quad (10)$$

ARA + BR'B type monomers: At any time in the reaction mass, three types of species will be present viz. P_n , the odd A-mers; Q_n , the odd B-mers; and S_n , the even-mers, as identified originally by Flory⁽¹⁾. Each species will have a distribution of its own.

The moments for the distributions are defined as follows

$$\overset{=(k)}{M}_P = \sum_{n=1}^{\infty} (2n-1)^k P_n ; \overset{=(k)}{M}_Q = \sum_{n=1}^{\infty} (2n-1)^k Q_n ; \overset{=(k)}{M}_S = \sum_{n=1}^{\infty} (2n)^k S_n \quad (1)$$

The reaction scheme for the three models are shown in Table A-2. The rate equations for various species and moments are shown in Tables A-3.1, A-3.2 and A-3.3 for batch reactors. The values at the reactor outlet will be obtained as in equations (6) and (8) above, the only difference is that 'x' and ' ' now defined as $x = k_p M_o t$ & $\theta = k_p M_o \tau \dots(12)$

In Model I, we assume that the monomer-monomer reaction rate constant is different from those for all other reactions, i.e. between monomers-polymers and polymers-polymers. In Model II we are assuming that the reactivity change due to the substitution effect is same for both the functional groups. In Model III we are assuming that the reactivity of one of the functional groups changes due to the substitution effect, but that of the other remains unaffected.

Table A-1Rate equations in ARB type polymerizationModel I

$$dz_1/dx = -(R-1)z_1^2 - M_o z_1$$

$$dz_2/dx = \frac{R}{2} z_1^2 - M_o z_2$$

$$dz_n/dx = \frac{1}{2} \sum_{m=1}^{n-1} z_m z_{n-m} - M_o z_n,$$

$$n = 3, 4, \dots$$

$$\frac{dM_o}{dx} = -\frac{(R-1)}{2} z_1^2 - \frac{M_o^2}{2}$$

$$\frac{dM_k}{dx} = (2^{k-1} - 1) z_1^2 + \frac{1}{2} \sum_{l=0}^k \frac{k!}{l!(k-l)!} M_l M_{k-l}$$

$$- M_k M_o, \quad k = 1, 2, \dots$$

Model II

$$dz_1/dx = -R z_1 M_o$$

$$dz_2/dx = \frac{R}{2} z_1^2 - (R-1) z_1 z_2 - M_o z_2$$

$$dz_n/dx = (R-1) z_1 z_{n-1} + \frac{1}{2} \sum_{m=1}^{n-1} z_m z_{n-m}$$

$$- (R-1) z_1 z_n - M_o z_n,$$

$$n = 3, 4, \dots$$

$$\frac{dM_o}{dx} = \frac{R-1}{2} z_1^2 - \frac{M_o^2}{2} - (R-1) M_o z_1$$

$$\frac{dM_k}{dx} = (1 - 2^{k-1})(R-1) z_1^2 + (R-1) z_1$$

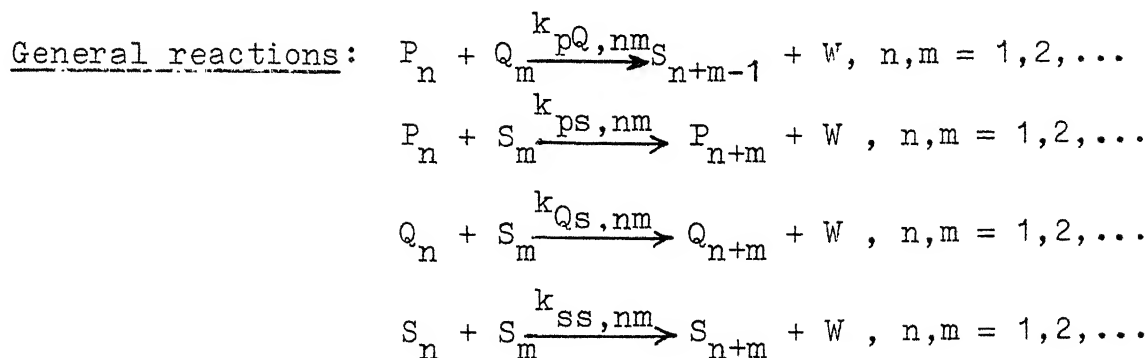
$$\sum_{l=1}^{k-1} \frac{k!}{l!(k-l)!} M_l$$

$$+ \frac{1}{2} \sum_{l=1}^{k-1} \frac{k!}{l!(k-l)!} M_l M_{k-l}$$

Initial conditions: at $x = 0$: $z_1 = 1, z_2 = z_3 = \dots z_n = 0$;

$$M_k = 1, \quad k = 0, 1, 2, \dots$$

Note: For definitions of the symbols see Nomenclature.

Table A-2Kinetic scheme for various ARA + BR'B polymerizationModel I

$$k_{pQ,11} = k_I; k_{pQ,1n} = k_p, n = 2, 3, \dots; k_{pQ,n1} = k_p, n = 2, 3,$$

$$k_{pQ,nm} = k_p; n, m = 2, 3, \dots$$

$$k_{ps,nm} = k_p, n, m = 1, 2, \dots$$

$$k_{qs,nm} = k_p, n, m = 1, 2, \dots$$

$$k_{ss,nm} = k_p, n \neq m, n, m = 1, 2, \dots$$

$$= k_p/2, n = m, n, m = 1, 2, \dots$$

Model II

$$k_{pQ,1m} = k_I; m = 1, 2, \dots; k_{pQ,n1} = k_I, n = 1, 2, \dots$$

$$k_{pQ,mn} = k_p; m, n = 2, 3, \dots$$

$$k_{ps,1m} = k_I; m = 1, 2, \dots; k_{ps,nm} = k_p, n = 2, 3, \dots; m = 1, 2, \dots$$

$$k_{qs,1m} = k_I; m = 1, 2, \dots; k_{qs,nm} = k_p; n = 2, 3, \dots; m = 1, 2, \dots$$

$$k_{ss,nm} = k_p; n \neq m, n, m = 1, 2, \dots$$

$$= k_p/2, n = m, n, m = 1, 2, \dots$$

Model III

$$k_{pQ,1m} = k_I, m = 1, 2, \dots; k_{pQ,nm} = k_p, n = 2, 3, \dots; m = 1, 2, \dots$$

$$k_{ps,1m} = k_I, m = 1, 2, \dots; k_{ps,nm} = k_p, n = 2, 3, \dots; m = 1, 2, \dots$$

$$k_{qs,nm} = k_p; n, m = 1, 2, \dots$$

$$k_{ss,nm} = k_p; n \neq m, n, m = 1, 2, \dots$$

$$= k_p/2, n = m, n, m = 1, 2, \dots$$

Rate equations for Model I in ARA + BR'B polymerization

$$\frac{dP_1}{dt} = -k_p (R-1) P_1 Q_1 - k_p P_1 (\bar{M}_Q^{(o)} + \bar{M}_S^{(o)})$$

$$\frac{dQ_1}{dt} = -k_p (R-1) P_1 Q_1 - k_p Q_1 (\bar{M}_P^{(o)} + \bar{M}_S^{(o)})$$

$$\frac{dP_n}{dt} = k_p \sum_{r=1}^{n-1} P_r P_{n-r} - k_p P_n (\bar{M}_Q^{(o)} + \bar{M}_S^{(o)}) \quad , \quad n = 2, 3, \dots$$

$$\begin{aligned} \frac{dQ_n}{dt} = k_p \sum_{r=1}^n P_r Q_{n-r+1} + \frac{1}{4} k_p \sum_{r=1}^{n-1} S_r S_{n-r} - \frac{1}{2} k_p S_n \bar{M}_S^{(o)} \\ - k_p S_n (\bar{M}_P^{(o)} + \bar{M}_Q^{(o)}) \quad , \quad n = 2, 3, \dots \end{aligned}$$

$$\frac{d\bar{M}_P^{(o)}}{dt} = \frac{d\bar{M}_Q^{(o)}}{dt} = -k_p (R-1) P_1 Q_1 - k_p \bar{M}_P^{(o)} \bar{M}_Q^{(o)}$$

$$\begin{aligned} \frac{d\bar{M}_S^{(o)}}{dt} = k_p (R-1) P_1 Q_1 + k_p \bar{M}_P^{(o)} \bar{M}_Q^{(o)} - \frac{1}{4} k_p \bar{M}_S^{(o)2} - k_p \bar{M}_S^{(o)} \\ (\bar{M}_P^{(o)} + \bar{M}_Q^{(o)}) \end{aligned}$$

$$\frac{d\bar{M}_P^{(k)}}{dt} = -k_p (R-1) P_1 Q_1 - k_p \bar{M}_P^{(k)} \bar{M}_Q^{(o)} + k_p \sum_{l=1}^k \frac{k!}{l!(k-l)!} \bar{M}_P^{(k-l)} \bar{M}_S^{(l)}$$

$$\frac{d\bar{M}_Q^{(k)}}{dt} = -k_p (R-1) P_1 Q_1 - k_p \bar{M}_Q^{(k)} \bar{M}_P^{(o)} + k_p \sum_{l=1}^k \frac{k!}{l!(k-l)!} \bar{M}_Q^{(k-l)} \bar{M}_S^{(l)}$$

$$\frac{d\bar{M}_S^{(k)}}{dt} = 2^k k_p (R-1) P_1 Q_1 + k_p \sum_{l=0}^k \frac{k!}{l!(k-l)!} \bar{M}_P^{(l)} \bar{M}_Q^{(k-l)}$$

$$+ \frac{1}{4} k_p \sum_{l=0}^k \frac{k!}{l!(k-l)!} \bar{M}_S^{(l)} \bar{M}_S^{(k-l)}$$

$$- \frac{1}{2} k_p \bar{M}_S^{(k)} \bar{M}_S^{(o)} - k_p \bar{M}_S^{(k)} (\bar{M}_P^{(o)} + \bar{M}_Q^{(o)})$$

Continued....

Table A3.1 (continued)

Initial conditions: at $t = 0$: $P_1 = P_{10}$; $Q_1 = Q_{10}$; $S_1 = 0$;

$$P_n, Q_n, S_n = 0 \quad , \quad n = 2, 3, \dots$$

$$\bar{M}_P^{(0)} = \bar{M}_P^{(1)} = \dots = \bar{M}_P^{(k)} = P_{10} ;$$

$$\bar{M}_Q^{(0)} = \bar{M}_Q^{(1)} = \dots = \bar{M}_Q^{(k)} = Q_{10} ;$$

$$\bar{M}_S^{(0)} = \bar{M}_S^{(1)} = \dots = \bar{M}_S^{(k)} = 0.$$

Table A3.2Rate Equations for Model II

$$\frac{dP_1}{dt} = -R P_1 \bar{M}_Q^{(0)} - R P_1 \bar{M}_S^{(0)}$$

$$\frac{dQ_1}{dt} = -R Q_1 \bar{M}_P^{(0)} - R Q_1 \bar{M}_S^{(0)}$$

$$\begin{aligned} \frac{dP_n}{dt} = & k_p (R-1) P_1 S_{n-1} + k_p \sum_{r=1}^{n-1} P_r S_{n-r} - k_p (R-1) P_n Q_1 - k_p P_n \bar{M}_S^{(0)} \\ & - k_p P_n \bar{M}_S^{(0)} \end{aligned}$$

$$\begin{aligned} \frac{dQ_n}{dt} = & k_p (R-1) Q_1 S_{n-1} + k_p \sum_{r=1}^{n-1} Q_r S_{n-r} - k_p (R-1) Q_n P_1 - k_p Q_n * \\ & (\bar{M}_P^{(0)} + \bar{M}_S^{(0)}) \end{aligned}$$

$$\begin{aligned} \frac{d\bar{M}_P^{(0)}}{dt} = & k_p (R-1) P_1 Q_1 - k_p (R-1) \bar{M}_P^{(0)} Q_1 - k_p (R-1) P_1 \bar{M}_Q^{(0)} \\ & - k_p \bar{M}_P^{(0)} \bar{M}_Q^{(0)} \end{aligned}$$

$$\begin{aligned} \frac{d\bar{M}_Q^{(0)}}{dt} = & k_p (R-1) P_1 Q_1 - k_p (R-1) \bar{M}_Q^{(0)} P_1 - k_p (R-1) Q_1 \bar{M}_P^{(0)} \\ & - k_p \bar{M}_P^{(0)} \bar{M}_Q^{(0)} \end{aligned}$$

Continued.....

$$\frac{d\bar{M}_S^{(0)}}{dt} = k_p (R-1) P_1 \bar{M}_Q^{(0)} - k_p (R-1) P_1 Q_1 + k_p (R-1) \bar{M}_P^{(0)} Q_1 \\ + k_p \bar{M}_P^{(0)} \bar{M}_Q^{(0)} - \frac{1}{4} k_p \bar{M}_S^{(0)2} - k_p (R-1) \bar{M}_S^{(0)} P_1 - k_p \bar{M}_S^{(0)} \\ [\bar{M}_P^{(0)} + \bar{M}_Q^{(0)}] - k_p (R-1) \bar{M}_S^{(0)} Q_1$$

$$\frac{d\bar{M}_P^{(k)}}{dt} = k_p (R-1) P_1 Q_1 + k_p (R-1) P_1 \sum_{l=1}^k \frac{k!}{l!(k-l)!} \bar{M}_S^{(l)} + k_p \sum_{l=1}^k \\ \frac{k!}{l!(k-l)!} \bar{M}_S^{(l)} \bar{M}_P^{(k-l)} - k_p (R-1) \bar{M}_P^{(k)} Q_1 - k_p (R-1) P_1 \bar{M}_Q^{(0)} \\ - k_p \bar{M}_P^{(k)} \bar{M}_Q^{(0)}$$

$$\frac{d\bar{M}_Q^{(k)}}{dt} = k_p (R-1) P_1 Q_1 + k_p (R-1) Q_1 \sum_{l=1}^k \frac{k!}{l!(k-l)!} \bar{M}_S^{(l)} \\ + k_p \sum_{l=1}^k \frac{k!}{l!(k-l)!} \bar{M}_S^{(l)} \bar{M}_Q^{(k-l)} - k_p (R-1) P_1 \bar{M}_Q^{(k)} - k_p \\ (R-1) Q_1 \bar{M}_P^{(0)} - k_p \bar{M}_P^{(0)} \bar{M}_Q^{(k)}$$

$$\frac{d\bar{M}_S^{(k)}}{dt} = -2^k k_p (R-1) P_1 Q_1 + k_p (R-1) P_1 \sum_{l=0}^k \frac{k!}{l!(k-l)!} \bar{M}_Q^{(l)} + k_p \\ \sum_{l=0}^k \frac{k!}{l!(k-l)!} \bar{M}_P^{(l)} \bar{M}_Q^{(k-l)} + k_p (R-1) Q_1 \sum_{l=0}^k \frac{k!}{l!(k-l)!} \bar{M}_P^{(l)} \\ + \frac{1}{4} k_p \sum_{l=0}^k \frac{k!}{l!(k-l)!} \bar{M}_S^{(l)} \bar{M}_S^{(k-l)} - \frac{1}{2} k_p \bar{M}_S^{(k)} \bar{M}_S^{(0)} - k_p (R-1) \\ \bar{M}_S^{(k)} (P_1 + Q_1) - k_p \bar{M}_S^{(k)} (\bar{M}_P^{(0)} + \bar{M}_Q^{(0)})$$

Initial conditions: Same as in Table A3.1.

Rate Equations for Model III

$$\frac{dP_1}{dt} = -R P_1 \bar{M}_Q^{(0)} - R P_1 \bar{M}_S^{(0)}$$

$$\frac{dQ_1}{dt} = -R P_1 Q_1 - k_p Q_1 (P_2 + P_3 + \dots) - k_p Q_1 \bar{M}_S^{(0)}$$

$$\frac{dP_n}{dt} = R P_1 S_{n-1} + k_p \sum_{r=2}^{n-1} P_r S_{n-r} - k_p P_n \bar{M}_Q^{(0)} - k_p P_n \bar{M}_S^{(0)}$$

$$\frac{dQ_n}{dt} = k_p \sum_{r=1}^{n-1} Q_r S_{n-r} - k_p (R-1) Q_n P_1 - k_p Q_n \bar{M}_P^{(0)} - k_p Q_n \bar{M}_S^{(0)}$$

$$\frac{d\bar{M}_P^{(k)}}{dt} = -k_p (R-1) P_1 \bar{M}_Q^{(0)} - k_p \bar{M}_P^{(k)} \bar{M}_Q^{(0)} + k_p (R-1) P_1 \sum_{l=1}^k$$

$$\frac{k!}{l!(k-l)!} \bar{M}_S^{(1)} + k_p \sum_{l=1}^k \frac{k!}{l!(k-l)!} \bar{M}_S^{(1)} \bar{M}_P^{(k-l)}$$

$$\frac{d\bar{M}_Q^{(k)}}{dt} = -k_p (R-1) P_1 \bar{M}_Q^{(k)} - k_p \bar{M}_Q^{(k)} - k_p \bar{M}_Q^{(k)} \bar{M}_P^{(0)} + k_p \sum_{l=1}^k$$

$$\frac{k!}{l!(k-l)!} \bar{M}_S^{(1)} \bar{M}_Q^{(k-l)}$$

$$\frac{d\bar{M}_S^{(k)}}{dt} = k_p (R-1) P_1 \sum_{l=0}^k \frac{k!}{l!(k-l)!} \bar{M}_Q^{(1)} + k_p \sum_{l=0}^k \frac{k!}{l!(k-l)!}$$

$$\bar{M}_P^{(1)} \bar{M}_Q^{(k-l)} + \frac{1}{4} k_p \sum_{l=1}^{k-1} \frac{k!}{l!(k-l)!} \bar{M}_S^{(1)} \bar{M}_S^{(k-l)} - k_p (R-1)$$

$$P_1 \bar{M}_S^{(k)} - k_p \bar{M}_S^{(k)} (\bar{M}_P^{(0)} + \bar{M}_Q^{(0)})$$

Initial conditions: Same as in Table A3.1.

CHAPTER A-3MATHEMATICAL COMPUTATIONS

In both APB type and ARA + BR'B type polycondensations we have used the four point Runge Kutta Gill method⁽³¹⁾ for predicting the batch concentrations. From these batch concentrations we have calculated the SCSTR outlet concentrations, using equations (6) and (8), by Simpson's rule⁽³²⁾, with a step size of $0.05 X$. For $R = 1.0$ when an analytical solution was possible, a check was made by using Laguerre quadrature⁽³³⁾. Each of the step by step integration starts at $X = 0$ and the value of each of the integrals (Equations (6) & (8)) is checked after every 400 step increments in X . The integration is stopped when it is found that even after 400 such steps the maximum change in the fastest growing integral is less than 0.5% of its present value. For APB type the convergence is decided on the basis the integral of the second moment as this is the fastest growing integral. For ARA + BR'B type polymerization the convergence criterion is based on sum of the integrals for 2nd moments of all three species. A check regarding accuracy was made by decreasing the step size which did not produce any significant difference.

After stopping the step by step integration, the actual values of the integrals are obtained by extrapolation. This is possible because the rate of growing of the values of each of the

integrals gradually decreases as 'X' increases until it becomes almost zero. This means that the integral values increase asymptotically and the final value is obtainable by ~~extra~~polation.

The integrals for monomer concentrations gives the average conversion in the outlet of SCSTR. Similarly average value of the first three moment integrals give the number average and weight average chain lengths from which the polydispersity index can be calculated.

CHAPTER A-4

RESULTS AND DISCUSSION

The parameter used in the study of ARB type polymerization is the ratio of the rate constants, ' R ' and in the study of $ARA + AR'B$, are both ' R ' and the initial molar fraction of the limiting reactant P, ' f_{Po} '. The weight distribution of the chain lengths for ARB polymerization at various values of θ and the reactivity ratio are shown for models I and II in figures 1 and 2. For the first kinetic model, it is observed that for $R > 1$, the MWD curves split into two as ' n ' decreases: one for odd values of n and the other, having higher weight fractions, for even values of n . This is expected because of the preferential reaction of monomer with itself thus giving a relatively larger rate of formation of the dimer. The unreacted monomer is very high in this case. In the second kinetic scheme, on the other hand, a splitting is obtained for $R < 1$. This can possibly be explained by the consideration that the reaction rate constant in dimer-dimer reaction is much higher than, say for example, between monomer and dimer (by which reaction is trimer is formed). These findings are same as obtained earlier for batch reactors^(21,22), and HCSTRs^(27,28) before.

The number average chain lengths and polydispersity indices for the two models of ARB polymerization in SCSTR are plotted in figs 3 to 6 as function of θ . For the sake of comparison, corresponding plots for batch and CSTR are included. Also, values obtained with $f_{PO} = 0.5$ for ARA + BR'B polymerization in SCSTR are included for comparison. The values for the latter ones are found to be always less than the corresponding ones in ARB polymerization. Usually the curves for SCSTR falls, as expected between the curves for batch and HCSTR.

In figures 7 and 8 are compared the values of polydispersity indices for the three different models of ARA + BR'B polymerization when the initial reactant ratio is other than 1:1. 'fPO' is the original fraction of the limiting reactant. From these plots it is seen that (i) the model II is most sensitive to the change in R values while model III is the least sensitive; this is shown by the fact that the change of ' ρ ' is maximum for a change in R values from R = 0.1 to 10.0, in case of model I. (ii) that in general for such a polymerization, the PDI value obtained for $R < 1$ are much higher compared to those obtained for $R > 1$ irrespective of the model and the fPO value. This possibly indicates that according to these models, for unequal initial concentrations of monomers, the dispersity of the polymer formed will be higher if there is a preferential polymer-polymer reaction as compared to the monomer-polymer reaction.

In figures 9 and 10 cross plots of \bar{P} vs monomer conversion for ARB type monomers, with constant chain length curves, are shown. These curves are of significant interest since they show the relationship between the three important parameters, conversion, chain length and polydispersity index. Here also it is seen that for same conversion \bar{P} falls as 'R' decreases.

In conclusion it may be observed that though the kinetic models that are proposed here are idealized they may be expected to simulate the polymerization reaction reasonably well under some conditions and for many classes of polymers. The results presented here are the outcome of a theoretical investigation and are given in the form of dimensionalized plots which can be used for study of particular classes of polymerization reactions. At least they can be used as a starting step while analyzing for more complex aspects of nonequal reactivity, provided more data are available.

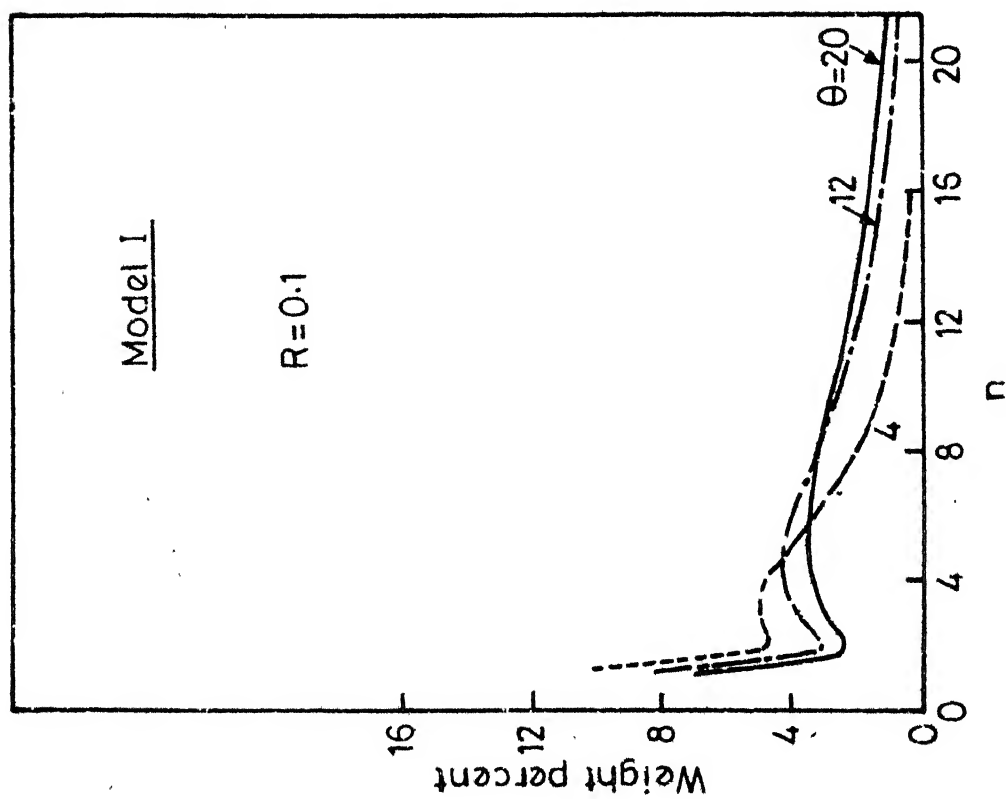
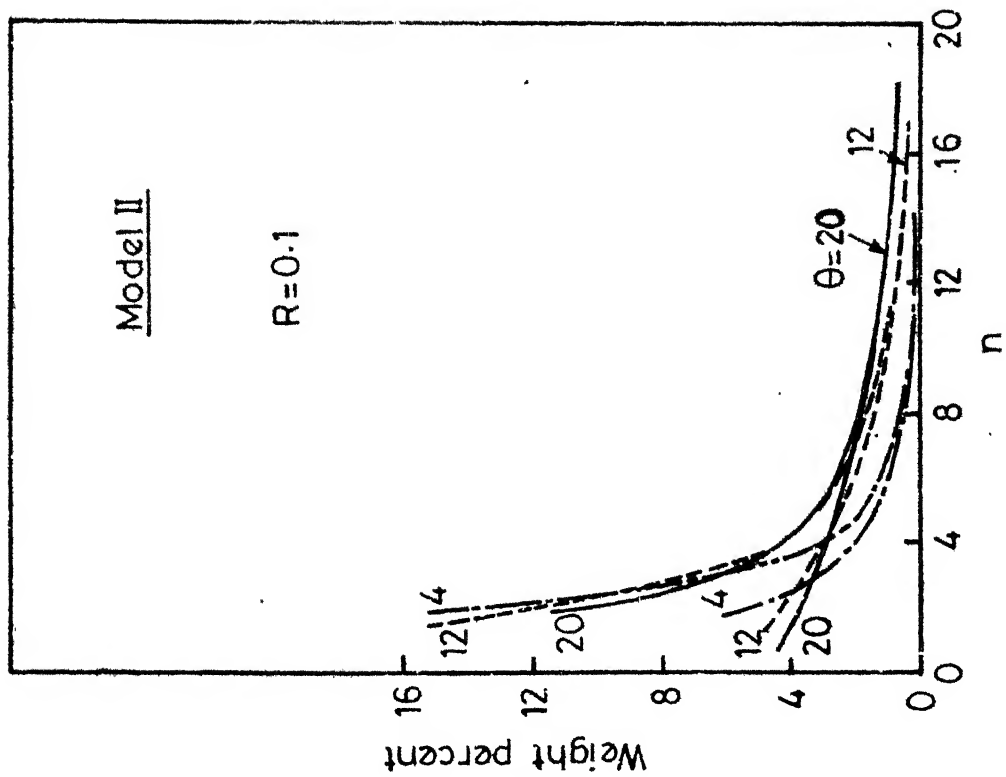


Fig. 1 - Weight distribution of chain lengths in ARB type polycondensation.

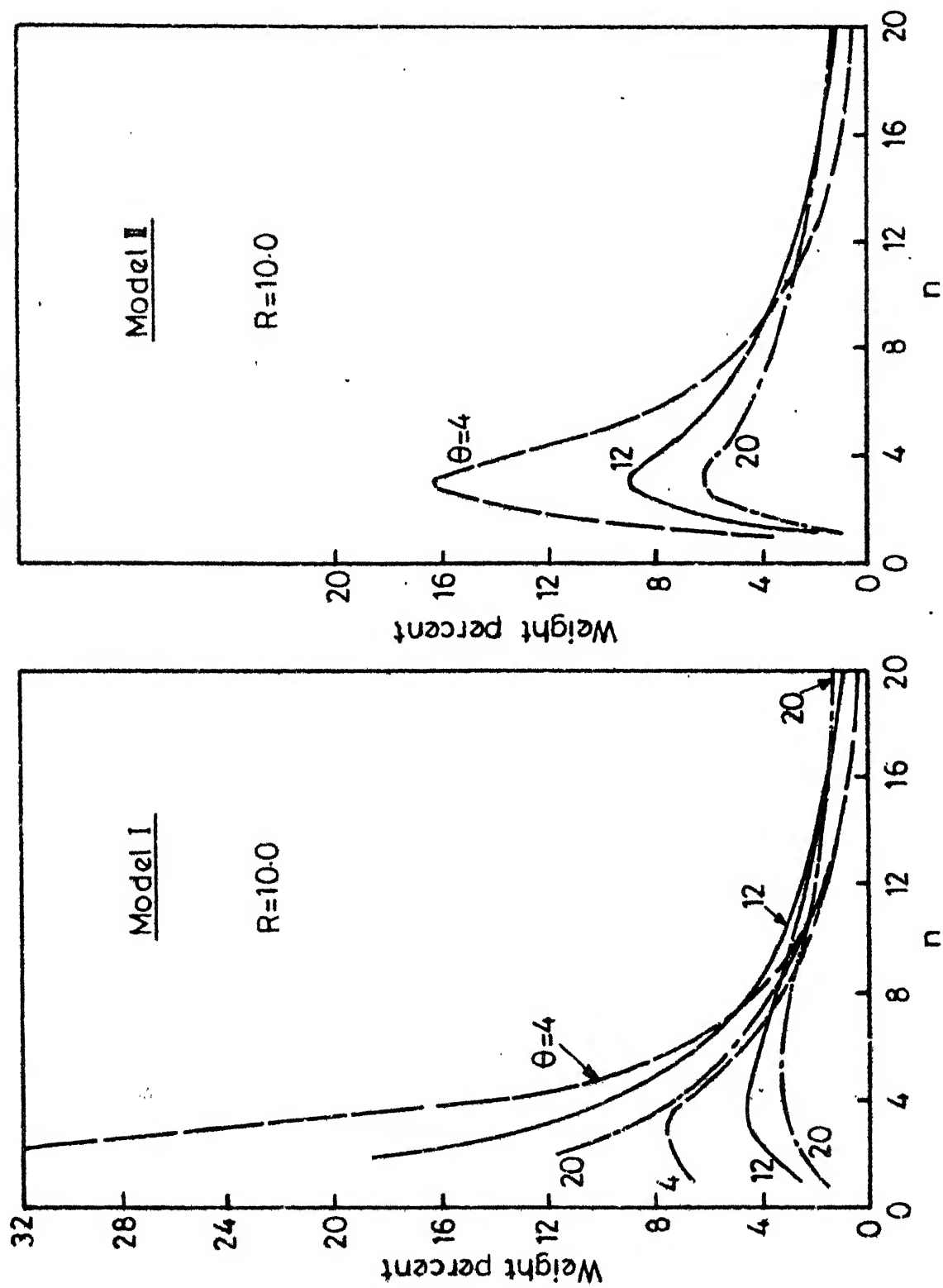


Fig. 2 - Weight distribution of chain lengths in ARB type polycondensation.

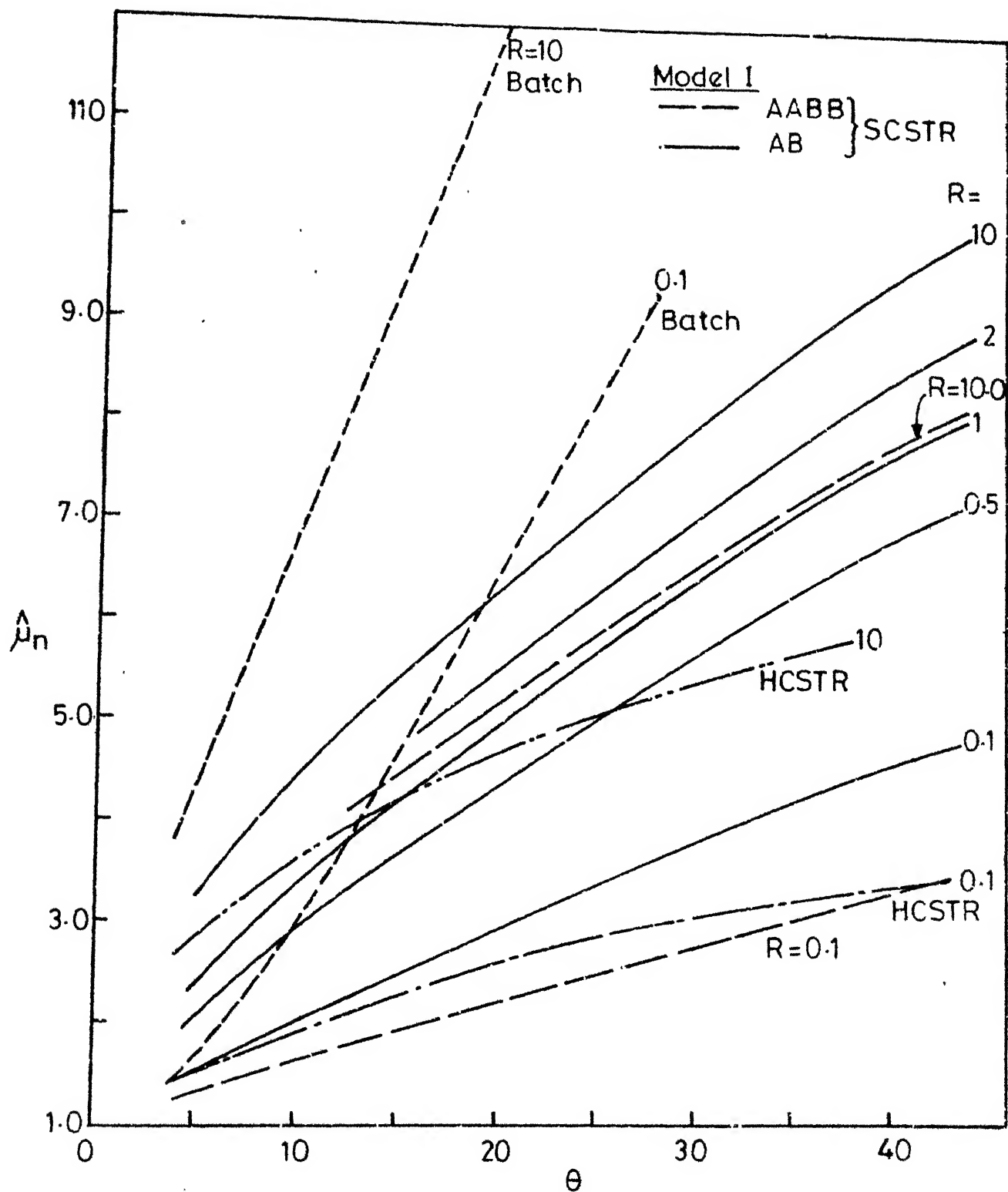


Fig. 3 - Chain length average vs. reactor holding time in ARB type & ARA+BRB polymerization.

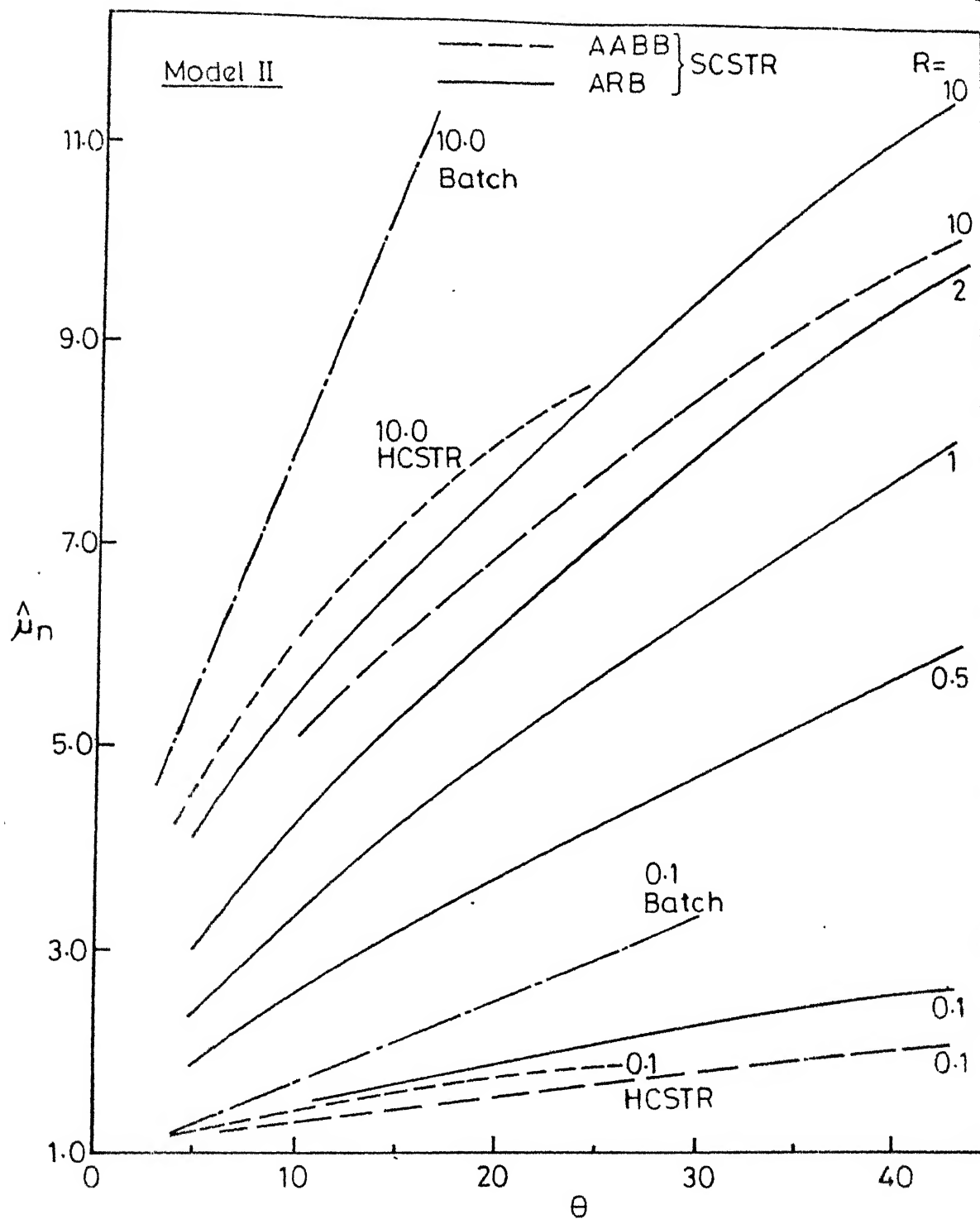


Fig 4 - Chain length average vs. reactor holding time in ARB type & ARA + BRB polymerization.

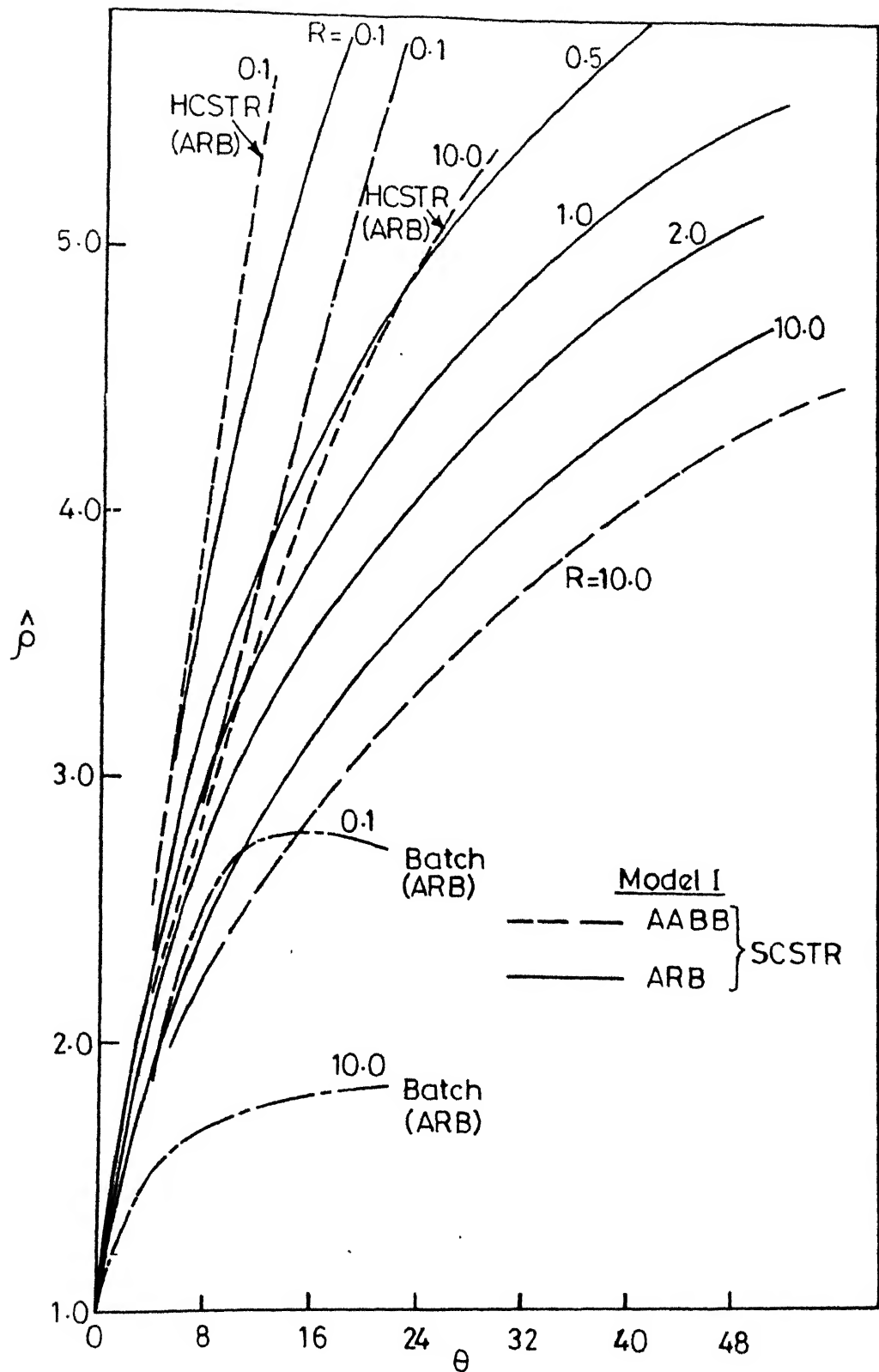


Fig. 5 - Polydispersity index vs. reactor holding time in ARB type & ARA + BRB polymerization.

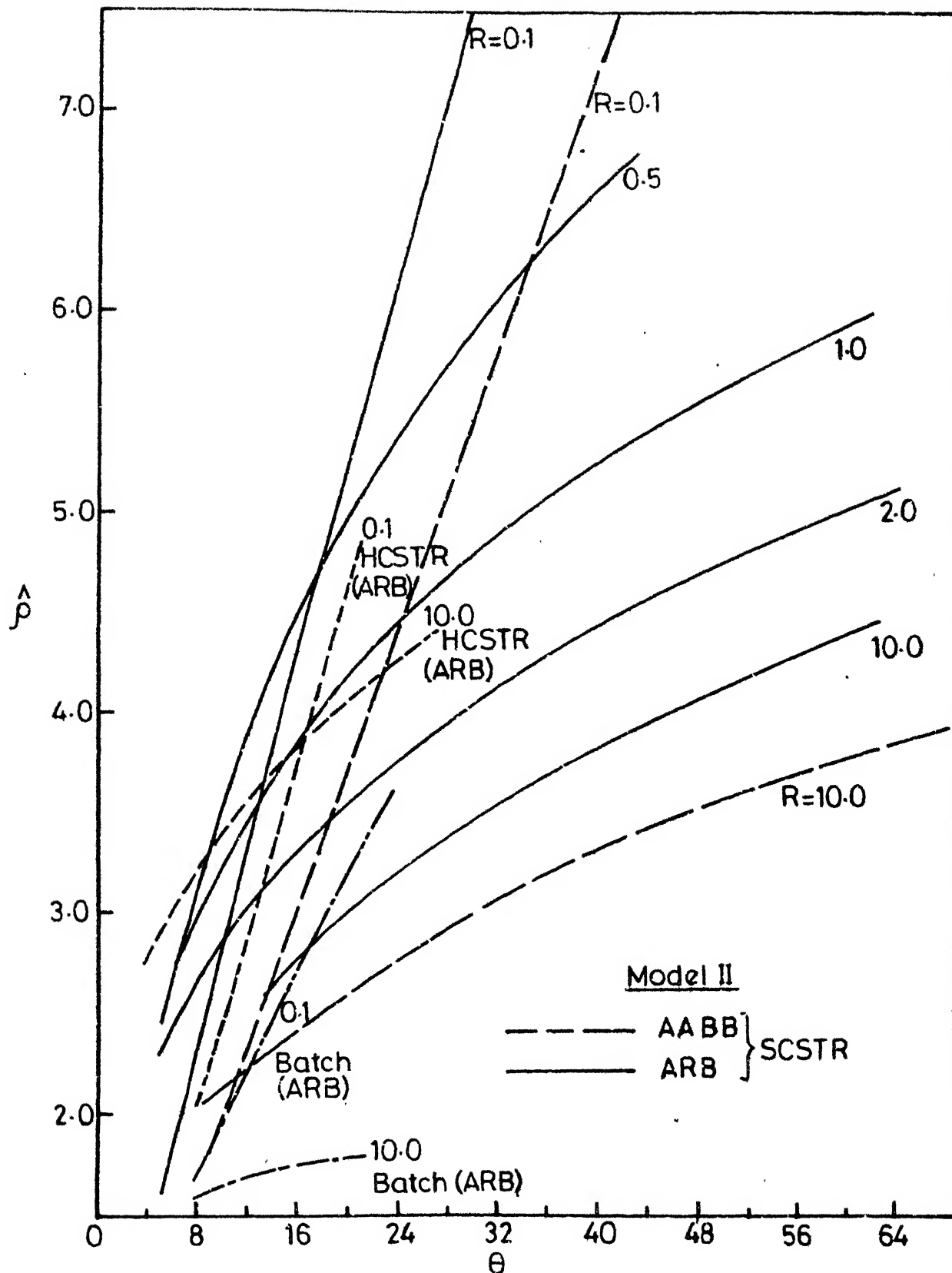


Fig. 6 - Polydispersity index vs. reactor holding time in ARB type & ARA + BRB polymerization.

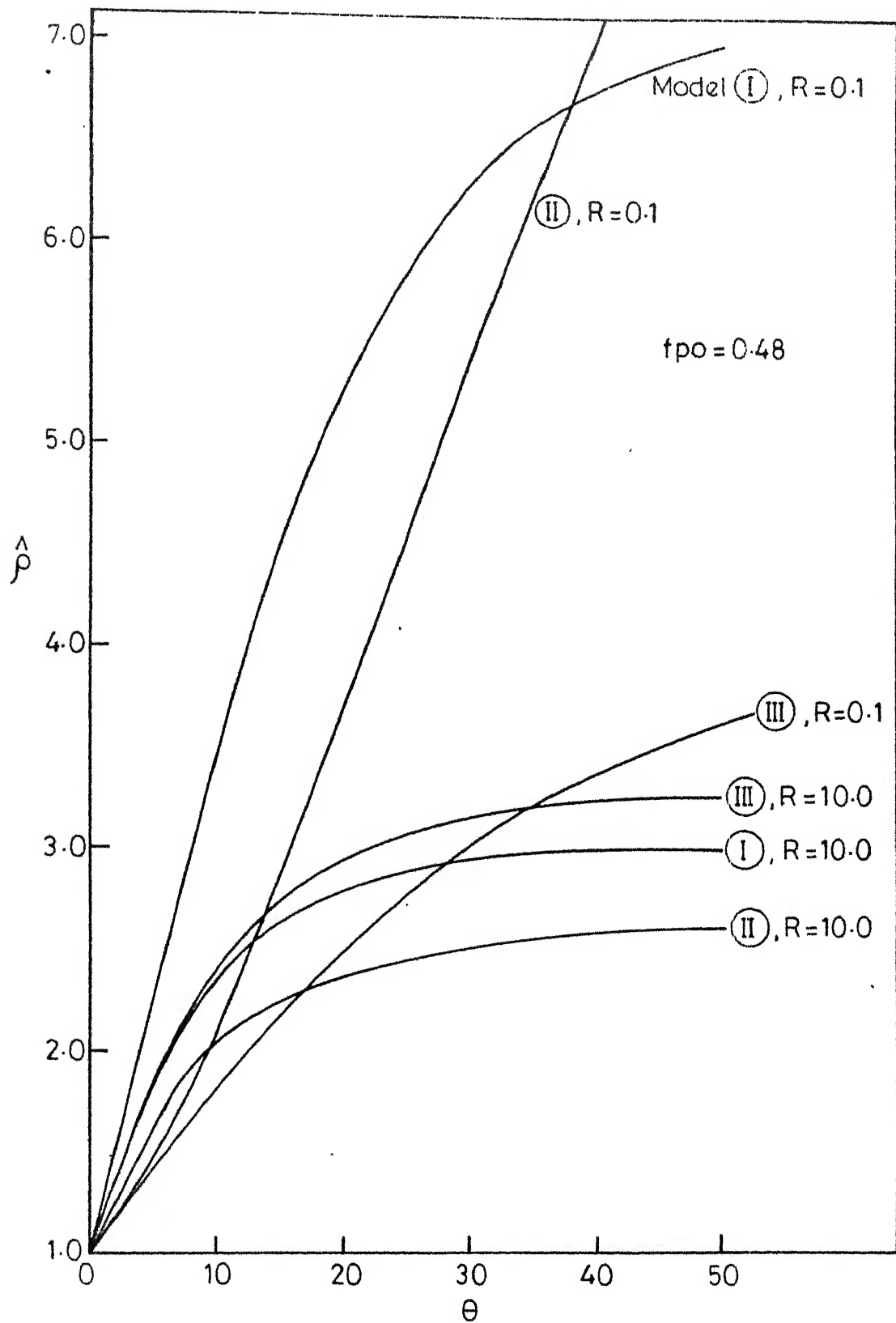


Fig. 7 - Polydispersity index vs. reactor holding time in ARA + BRB polymerization.

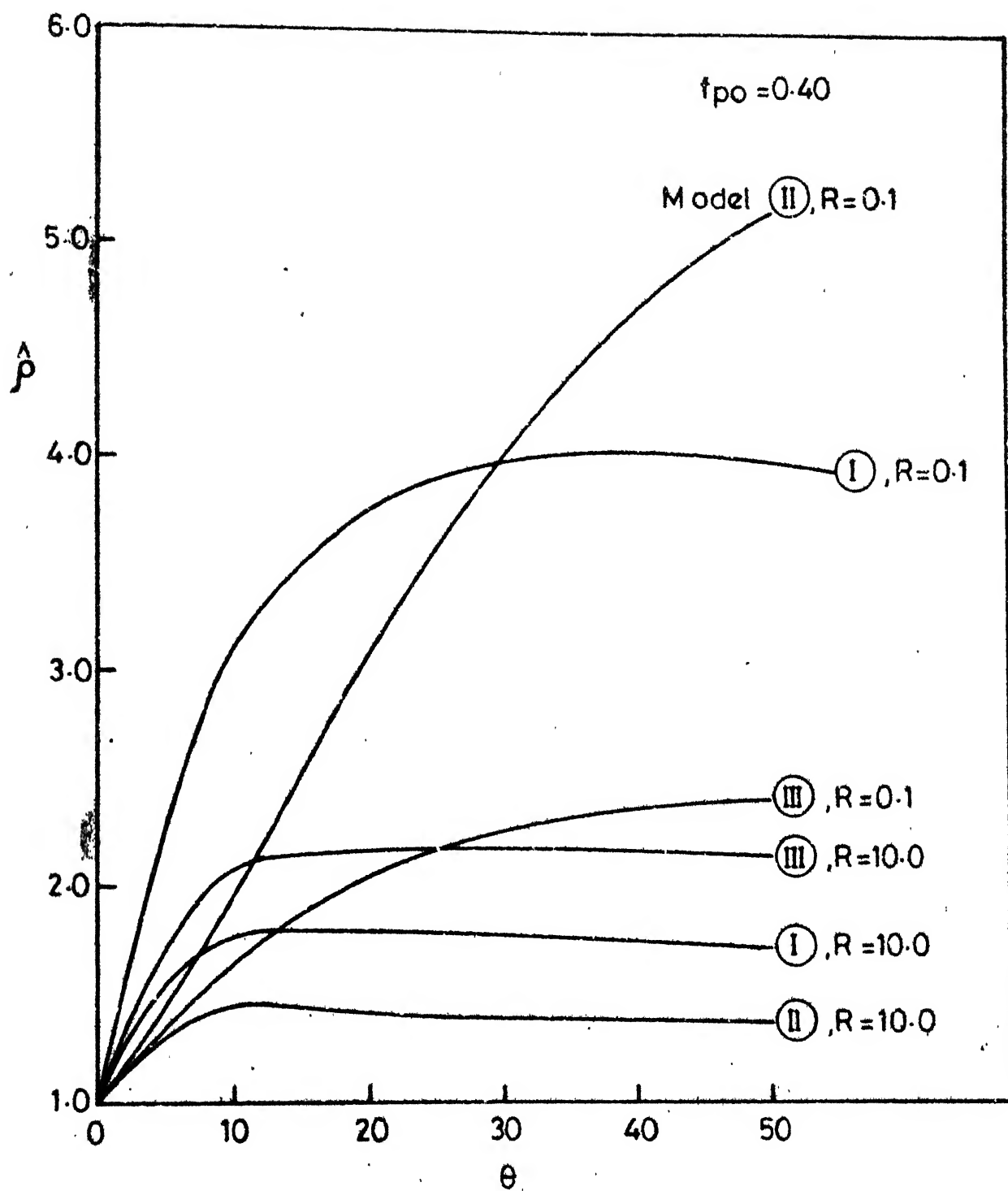


Fig. 8 - Polydispersity index vs. reactor holding time in ARA + BRB polymerization.

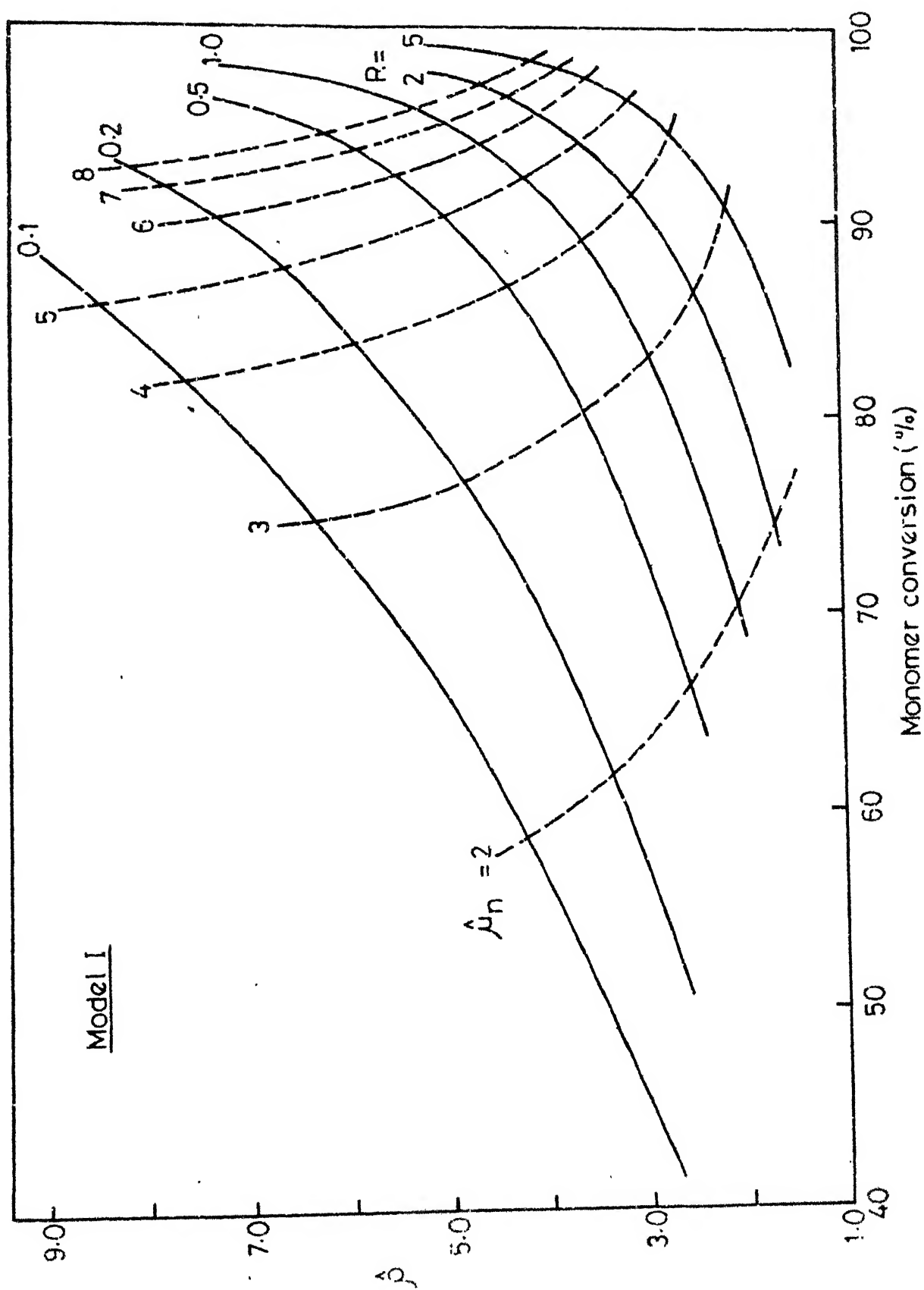


Fig. 9 - Cross plot of polydispersity index vs. monomer conv. including constant chain length curves.

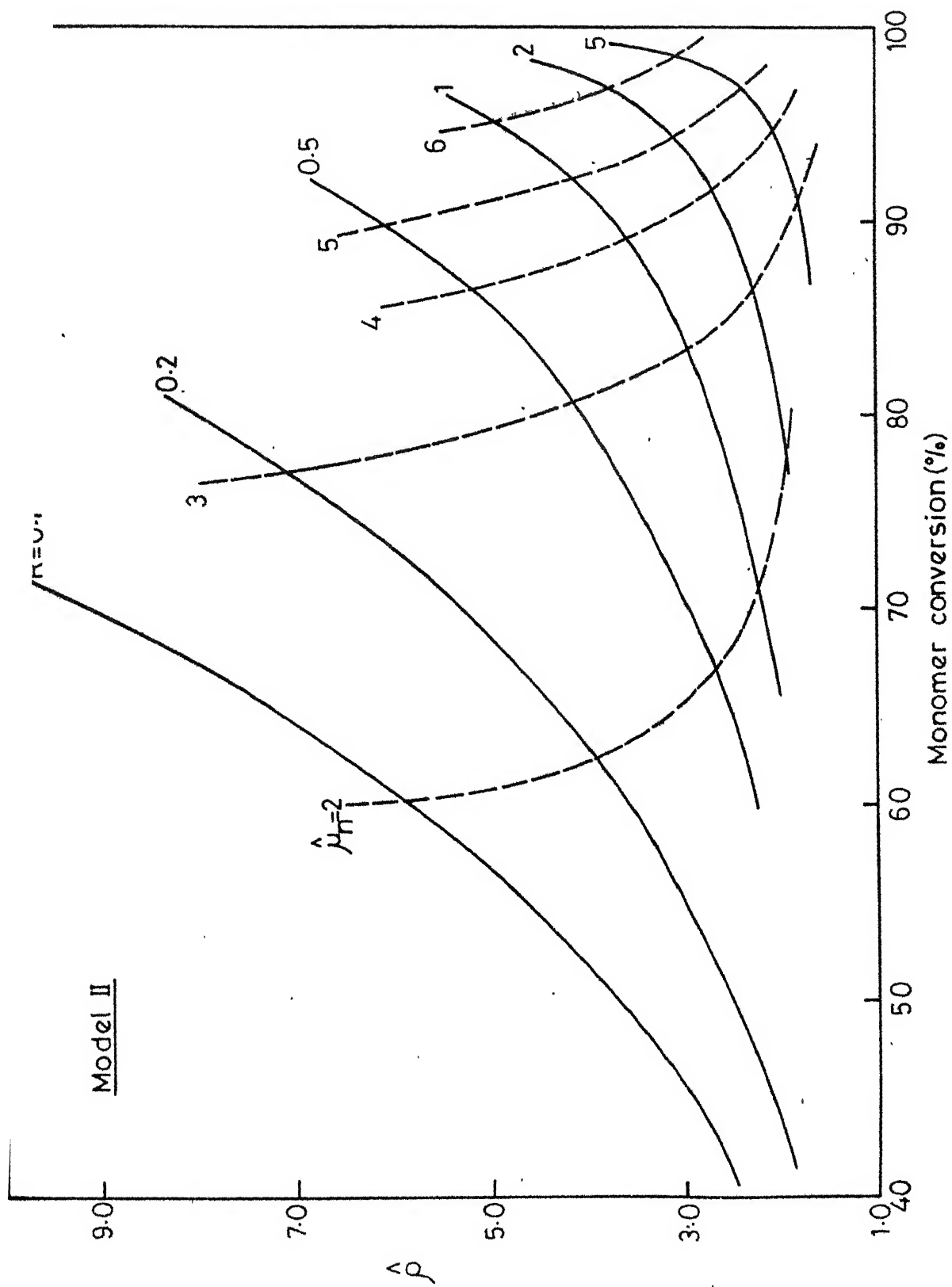


Fig. 10 - Cross plots of polydispersity index vs. monomer conv. including constant chain length curves.

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PART B

STUDIES ON THE POLYMERIZATION OF NYLON 6

CHAPTER B-1

Introduction to Nylon-6

Nylon-6, which is the generic term for a synthetic linear polyamide in which the repeating unit of the chemical structure contains six carbon atoms, $\text{—CONH—(CH}_2\text{)}_5\text{—}$, is produced by the ring-scission polymerization of the cyclic monomer ϵ -caprolactam. The chemistry of Nylon-6 polymerization has been comprehensively reviewed by Reimschuesel⁽¹⁾. Polycaproamide can be produced from caprolactam by one of three entirely different routes viz., hydrolytic polymerization, cationic polymerization and anionic polymerization. The cationic and anionic cases are only of theoretical interest^(1,2-6), but the hydrolytic polymerization is by far the most important commercial process for Nylon-6 production. The actual plant practice may vary depending on local conditions and demands, but the basic process remains the same^(1,7-8). Most of the commercial processes consist of a feed section where carefully controlled compositions are obtained containing molten caprolactam, water, acids or bases and other necessary additives. The bulk of the reaction takes place in the polymerization reactor, the product from which is treated for removal of unreacted monomer and low molecular weight cyclic oligomers either by hot water extraction or by vacuum evaporation. The monomer recovered is recycled and the polymer is sent to the processing section.

Many variations in the process conditions and the reactor designs have been investigated^(1,9,10). Analysis and simulation of different polymerization reactor systems have been carried

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out by different workers^(6,9-12) and based on these information some optimization studies have also been made^(10,13,14).

Besides the existing processes reported in the literature^(1,10), some novel operations have been patented recently⁽²⁴⁻²⁹⁾. Many process modifications have been suggested also to increase the process efficiency^(15,16), to improve the product properties⁽¹⁷⁻¹⁹⁾ and for better removal of monomer and low cyclics⁽²⁰⁻²³⁾.

In our present study, all the major established reactions involved with the hydrolytic polymerization of caprolactam have been taken into consideration. Based on the available information on reaction kinetics and polymerization mechanism and partly with a semi-empirical approach, equations for three sets of molecular weight moments have been developed, corresponding to the three different species present viz., the bifunctional chains, the monofunctional chains and the closed macrorings. From these three sets of moments it should be possible to get all the necessary information about the monomer conversion, molecular weight distribution and their averages for all kinds of species at every stage of polymerization.

Hydrolytic Polymerization of Nylon-6

Kinetics and Equilibrium Studies: The course of reaction during polymerization of caprolactam can be followed by the end group determination as suggested by Willoth⁽³⁰⁾. Studies have been made on the polymerization kinetics by Hermans et.al.⁽³¹⁾, Kruissink et.al.⁽³²⁾, Heikens et.al.⁽³³⁾, Willoth^(34,35), Dorr and Willoth⁽³⁶⁾, Tai et.al.^(37,53) for hydrolytic polymerization with or without the presence of acids or amines. Studies on polymerization equilibrium and effect of process conditions on the MWD of equilibrium polymerization have been reported by Fukumoto⁽³⁸⁾, Majury⁽³⁹⁾, Tobolsky and Eisenberg⁴⁰, Reimschuessel⁽⁴¹⁾, Reimschuessel and Dege⁽⁴²⁾ and Smith⁽⁴³⁾.

Mechanism of Polymerization: On the basis of the kinetic and equilibrium investigations made so far it has been established that the hydrolytic polymerization involves three major equilibrium reactions, namely,

- i) ring opening reaction, where the monomer, the caprolactam ring, is opened up by water molecules under proper reaction conditions, to form amino caproic acid, the shortest bifunctional chain,
- ii) polycondensation reaction, where the amino and carboxylic acid end groups in linear bifunctional chains react with one another to form larger chains via amide linkages, with water as the condensation product; and

iii) poly addition reaction, where the monomer caprolactam adds directly to any of the growing linear chains as in a typical chain growth polymerization⁴⁴. Poly addition is the primary reaction during the polymerization process and is mainly responsible for the conversion of caprolactam. But in the later stages of polymerization linear poly condensation becomes important since this reaction determines the final molecular weight distribution in the product, as equilibrium is approached.

Besides these three, two more reversible reactions have been identified. One, the so called termination, is the reaction of bifunctional linear chains with monofunctional acids or amines, which are most commonly used as chain stabilizers⁽⁴⁵⁾, to form monofunctional long chains. The other reaction, known as cyclization, is a transamidation by which the end group of long poly caproamide chains attacks its own amide linkages, by what is termed as 'back biting', to form shorter linear chains and macro rings of moderate molecular weights. This reaction will again be discussed later.

Cyclic Oligomers: In the equilibrium polymer of Nylon-6, some low molecular weight macrocyclic compounds are always found. Though their concentrations are rather low, the removal of these compounds from the polymer is essential prior to processing, since their presence adversely affects the processing of the polymer and its physical properties. For this reason these compounds have been subject to considerable investigations.

detection
 Their \angle and quantitative estimation has been done by many workers^(47,53). Mochizuki and Ito⁽¹¹⁾ have reported cyclic oligomer concentration as a function of reaction time during polymerization. Based on the ring-chain equilibrium concept of Jacobson and Stockmayer⁽⁵⁴⁾, Semlyen and Walker⁽⁵⁵⁾ had attempted, using the Flory-Williams rotational isomeric state model, to predict theoretically the percentage of low cyclic oligomers in Nylon-6 equilibrium melt, though the comparison with experimental data is inconclusive. Andrews et al⁽⁴⁸⁾ have reported experimentally determined equilibrium concentrations of cyclic oligomers up to the hexamer and the corresponding equilibrium constants for cyclization reaction. They also described the effect of post polymerization treatment on their concentration. Reimschuessel⁽¹⁾ has attempted to curve fit these equilibrium constants as a function of the ring lengths and temperature.

Rate and Equilibrium Constants: Reports on the investigation of reaction kinetics of caprolactam polymerization have shown that each of the ring opening, polycondensation and polyaddition reactions are catalysed by $-\text{COOH}$ end groups^(1,31,33), though the actual dependence of rates on catalyst concentration is not established rationally. In the usual empirical approach the forward reaction rate constants of these reactions are thought, as a first approximation, to consist of two parts, one of which is linearly dependent on $-\text{COOH}$ group concentration, and the other independent as follows:

$$k_1 = k_1^O + c k_1^C \quad (31) \quad (1)$$

where 'i' designates either of the above three reactions, 'c' is the acid end group concentration; k_i^o and k_i^c are similar to Arrhenious reaction rate constants, each being determined by a frequency factor and an activation energy e.g.

$$k_i^j = A_i^j \exp (- E_i^j / RT) \quad (2)$$

where superscript 'j' is either 'o' or 'c'. The equilibrium constants K's for these three reactions have been determined from thermodynamic quantities ' ΔH ' and ' ΔS ' and many reports agree quite well. The relationship is

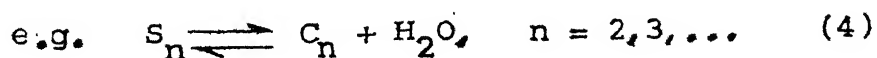
$$K_i = \exp \left(\frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT} \right) \quad (3)$$

To completely specify the kinetics, one thus needs to know A_i^j , E_i^j , ΔS_i and ΔH_i as given in Reimschuessel⁽¹⁾. Recently, however, Tai et al^{37,56} have determined these values independently, using least squares curve-fitting and though their reported numerical values sometimes differ substantially from Reimschuessel's values, they are claimed to produce less deviation from their extensive experimental data.

Mochizuki and Ito⁽¹¹⁾ in their model, have tried to show that the forward reaction rate constant in the reaction with monofunctional acid depends on $-COOH$ concentration as well as the melt viscosity, though their data show that the viscosity dependence is quite small. In our case, we will consider that the reactivity of an end group in a monofunctional chain, for example, is the same as that in a bifunctional chain.

In the cyclization reaction also, Mochizuki and Ito⁽¹¹⁾ have taken an entirely different approach which is not quite unquestionable. They have used, for a cyclization reaction,

the reaction between the $-NH_2$ and group and $-COOH$ end group of the same chain, with production of one water molecule and a macroring of the same length:



They did not consider the attack on mid chain amide linkages by end groups, which is the general cyclization reaction. Moreover, their data for the rate constants are not published due to proprietary reasons. In the present case we have used a different cyclization reaction scheme and as a matter of fact, we have not considered the above reaction of Mochizuki and Ito at all. The reason is if we consider the above reaction with the same theoretical approach as in the other reactions, it is imperative that we consider the ring opening of macrorings also, as it is a reversible reaction. But, except Tai et.al.⁽⁵³⁾ who considered ring opening of the dimer, no data are available in the literature for such a reaction. Hence, we have kept it out of consideration. However, we can partially justify it by considering the fact that the probability for this reaction would always be the least among all other cyclization reactions for the same chain length because it involves complete end to end bending of the polymer chain. In our model we have been forced to make certain simplifications on the original model of Jacobson and Stockmayer⁽⁵⁴⁾ in order to make it amenable to mathematical treatment. In a semi-empirical approach we have taken the cyclization equilibrium constant to vary inversely with the length of the macroring formed. We will consider it in some detail in the next chapter.

MWD: Theoretical studies on the molecular weight distribution in polycaprolactam has been relatively fewer. Willoth⁽⁵⁷⁾ and Hermans et.al.⁽⁵⁸⁾ have tried to match the MWD in polycaprolactam to a Flory-Schulz distribution with relatively little success, this is more so in the later stages of polymerization. Tirrel et.al.⁽⁶⁾ simulated the polymerization of caprolactam, in different PFR-CSTR combinations, under some simplifying assumptions (and with some errors) and reported the theoretically predicted MWD averages. Tai et.al.⁽⁵⁹⁾ recently tried to predict MWD averages theoretically with an assumption of Schulz-Zimm distribution, and found polydispersity indices from GPC about 9% higher than computed values.

In our work we will be making use of an approach suggested by Krishnan⁽¹²⁾ and Gupta and Gandhi⁽⁶¹⁾ which is based on the method of Min⁽⁶⁰⁾. Krishnan has simulated some CSTR-PFR combinations for Nylon-6 polymerization and has reported the MWD averages, while Gupta and Gandhi have suggested a general method for getting the actual MWD as well. The mathematical method used by them is computationally efficient, but in none of the above works the cyclization reaction has been included, which we will be doing here.

In this context, references to two other recent works may be made, though they are not particularly related to Nylon-6. In the first, Howell et.al.⁽⁶²⁾ attempts to get a semiempirical distribution function for linear and circular Gaussian chains; and in the second, Sicotte⁽⁶³⁾ uses a Gram-Charlier series expansion of molecular weight distribution. This latter approach

is in many ways similar to that used by us, but comparatively more difficult computationally and there is no evidence that it is guaranteed to work for Nylon-6 system.

CHAPTER B-3

Reaction Simulation

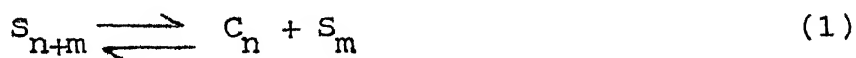
Reaction Scheme: The present reaction scheme which includes all five reactions identified so far in Nylon-6 polymerization was first proposed by Gupta et.al.⁽⁶⁴⁾. The reaction scheme is presented in Table B-1. At any time in the reaction mixture, there would be three kinds of species; e.g. bifunctional chains, denoted by S_n , $n=1,2,\dots$; monofunctional chains, denoted by A_n , $n = 1,2,\dots$, and rings, denoted by C_n , $n = 1,2,\dots$. Initial feed is composed of ' C_1 ' (i.e. the monomer); water, designated by ' W ', and ' A_1 ', the stabilizer (usually monofunctional acid, e.g. $ROOH$, where ' R ' is a nonreactive group). The rate constants k_1 , k_2 , k_3 , k_1' , k_2' and k_3' are based on the concentration of the functional groups like $-COOH$, $-NH_2$ and $-CONH-$ etc. and these are the ones reported in the literature⁽¹⁾. In writing rate equations for molecular species, we have to account for all the reactions occurring.

- i) for ring opening reaction, rate equations are directly obtained for molecular species, e.g. C_1 .
- ii) for condensation reaction, in the forward reaction, ^{constant} would be $2k_2$, as there are two possibilities, the $-COOH$ of S_n may react with $-NH_2$ of S_m and vice versa, unless n and m are equal, when it would be k_2 ^(64,65). In the reverse reaction, the rate constant will usually be $2k_2'$, because a water molecule can attack a linear chain S_{n+m} at two

places to give exactly similar products; the rate constant will however be k_2' if $(n+m)$ is even and the central amide linkage is attacked.

- iii) for reaction with monofunctional acids, the forward reaction rate constant is always k_2 , as only one $-NH_2$ on S_n may react with one $-COOH$ of A_m . The reverse reaction rate constant will always be k_2' , because the reaction between W and A_{n+m} gives different products when water attacks the i -th and the $(n+m-i)$ th amide linkages.
- iv) in the general polyaddition step, since the $-NH_2$ end groups of S_n can react with any of the 'm' amide linkages in a cyclic m-mer, the rate constant is mk_3 . In the cyclization step, the $-NH_2$ end group of S_{n+m} can attack any of the $(n+m-1)$ $-CONH-$ groups on itself to give several products; the rate constant for this reaction depending on the size of the macro-cyclic formed (C_i) and denoted by $k_3'(i)$.

The cyclization reaction rate constants require special consideration here. First of all let us establish the relation between this cyclization reaction and that originally dealt with by Jacobson and Stockmayer⁽⁵⁴⁾, i.e.



It should be noted that these two reactions are of opposite nature; i.e. the way the reactions have been defined, the forward reaction of the first is equivalent to the reverse reaction in the second, the difference being that the former reaction considers equilibrium between all the chains and rings at

a time, while the latter concentrates on a single chain in equilibrium with a ring of a particular size. It has been shown⁽⁵⁴⁾ that the equilibrium constant for reaction (1), K_A , defined as

$$K_n = (S_m \cdot C_n) / S_{m+n} \quad (2)$$

can be expressed as

$$K_n = C_n / x^n \quad (3)$$

where 'x' is the fraction of reacted end groups in the chain fraction. Now if we consider our present cyclization equilibrium it is easy to establish that

$$\frac{nk_3}{k_3(n)} = \frac{\sum_{m=1}^{\infty} S_{n+m}}{C_n \sum_{m=1}^{\infty} S_m} = \frac{1}{C_n} \cdot \left(1 - \frac{\sum_{m=1}^n S_m}{\sum_{m=1}^{\infty} S_m} \right) \quad (4)$$

Defining an equilibrium constant $K_3(n)$ for the present case as $K_3(n) = k_3/k_3(n)$, we get

$$K_3(n) = \frac{1}{n C_n} \left(1 - \frac{\sum_{m=1}^n S_m}{\sum_{m=1}^{\infty} S_m} \right) = \frac{1}{n K_n x^n} \left(1 - \frac{\sum_{m=1}^n S_m}{\sum_{m=1}^{\infty} S_m} \right) \quad (5)$$

It should be noted that the concentrations S_m and 'x' are the equilibrium values. Hence x is very nearly unity. So from eqn. (5) it may be concluded that at least for small values of 'n', it may be written, without much error, as

$$K_3(n) \simeq \frac{1}{n K_n} \quad (6)$$

Now for $n = 1$, K_n is the equilibrium constant for the reaction $C_1 + S_n \rightleftharpoons S_{n+1}$. This value has been investigated by many

workers and agree reasonably well⁽¹⁾.

The values of K_n for $n = 2$ to 6 are reported in the literature^(1,48). values for $n > 6$ are not available because it's not possible to detect and quantitatively measure the concentration of C_n in equilibrium polymer beyond $n > 6$. From the data of K_n vs. n , it is shown that fortunately the functionality can often be expressed as

$$K_n = \frac{B}{n^2}, \quad n = 2, 3, \dots \quad (7)$$

where B is a constant. As an example ' B ' is approximately 0.1692 at 235°C ⁽⁶⁴⁾. Thus from (6) and (7), one gets

$$k_3^1(n) = \frac{k_3 * B}{n}, \quad n = 2, 3, \dots \quad (8)$$

We have assumed that this functionality between $k_3^1(n)$ and n is retained for values of n greater than 6 . As will be seen later, this functionality is a very convenient form which enables us to adopt the moment approach. For any functionality relationship other than that in (8), a moment analysis becomes extremely difficult.

Rate Equations: The reaction mechanism having been established, we may now proceed to write the rate equations for various species present in the reaction mass. The rate equations for a batch reactor or PFR are shown in Table B-2. For a CSTR, the derivatives on the LHS of these equations will be replaced by the difference in input and output concentrations divided by the reactor holding time. Because of the reversibility of the reactions, it may be seen that the solution for any species,

say S_n , will require knowledge of the concentrations of all three species A, C and S, longer than 'n'. For this reason, the analysis becomes, at least theoretically, the solution of an infinite set of equations. Were it possible to solve all of these coupled differential equations (or algebraic equations, as the case may be), all the necessary information about the polymerization could have been obtained. Gupta et.al.⁽⁶⁴⁾ have integrated this set of equations for batch reactors and have reported the results in the form of molecular weight distributions and their averages, for both chains and rings, as function of reaction time. However, as is expected, this approach takes disconcertingly a large computation time, which is quite natural because of the necessity of handling of literally hundreds of coupled differential equations. This has motivated search for more computationally efficient mathematical approaches even at the expense of some accuracy, if necessary! The moment approach which will now be described is undertaken with this view in mind. This approach will presumably be more useful in case of CSTR's, since it will be extremely difficult, to solve so many algebraic equations efficiently.

Moment equation: As has just been stated, to make a rigorous and accurate analysis of the polymerization reaction, one needs to handle, at least theoretically, an infinite number of equations. The idea in the moment approach is to convert this infinite set of equations to a set of reasonably small number of moment equations so that the analysis becomes easier.

As has been previously described there are three kinds of species in the polymerizing mixture; bifunctional chains (S_n), monofunctional chains (A_n) and rings (C_n); and each of these species will have a weight distribution of its own.

Let us define three sets of moments as follows:

$$\lambda_k = \sum_{n=1}^{\infty} n^k S_n, \quad \gamma_k = \sum_{n=1}^{\infty} n^k C_n$$

and

$$\beta_k = \sum_{n=1}^{\infty} n^k A_n \quad (9)$$

If we multiply the rate equation for any species, say S_n , by n^k , and sum up the resulting equations for $n=1$ to ∞ , we should get the rate equations for $d\lambda_k/dt$. The same method applies for the A_n 's and C_n 's. After considerable mathematical manipulations one arrives at the set of equations given in Table B-3. Note that no expression is available for $d\gamma_0/dt$, because that involves summation of a harmonic series. Also note that $\frac{d\lambda_1}{dt} + \frac{d\beta_1}{dt} + \frac{d\gamma_1}{dt} = 0$, which is expected since $\lambda_1 + \beta_1 + \gamma_1 = \text{constant} = C_{10} + a_0$.

To integrate the rate equations for the moments it is necessary to get explicit rate equations instead of those involving series summations as shown in the above equation. In order to do it, recurrence formula for these series summations are necessary. Appendix B-1 lists some of these series sums.

Samples of individual moment rate equations are shown in Appendix B-2. Using the series summation formula listed in Appendix B-1, any other moment rate equation can be similarly obtained.

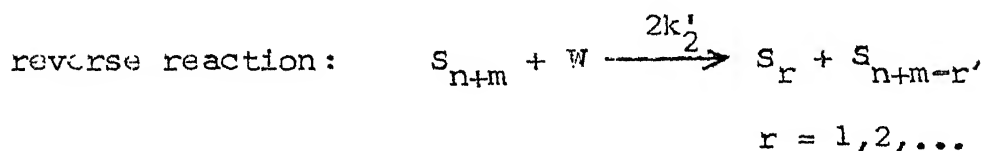
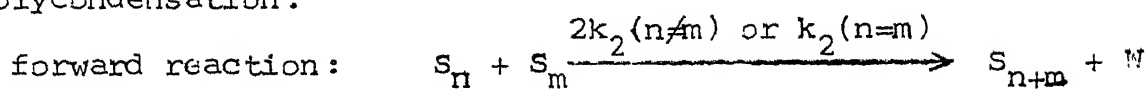
It should be noted that the rate equation for the k -th moment requires the knowledge of the $(k+1)$ th moment. Our subsequent approach is to search for a mathematical tool using which one can express the $(k+1)$ th moment in terms of the k -th moment, and get the actual molecular weight distribution from these moments. This method will be described in the next chapter.

Once we are in a position to express the $(k+1)$ th moment in terms of the k -th moment, we can integrate the above set of differential equations until equilibrium is reached. The results thus generated will give all the necessary information; and after a sound mathematical method is established, one may possibly use this technique for an efficient reactor simulation purpose and for subsequent optimization studies. However, that is beyond our scope.

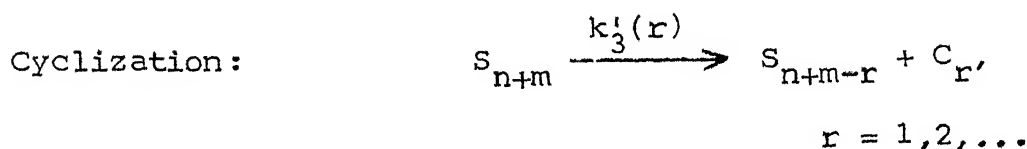
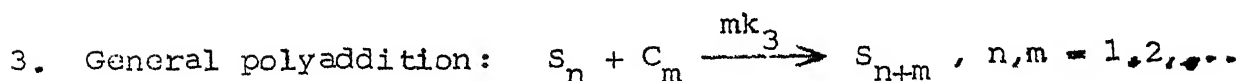
Table B-1

Kinetic scheme for nylon 6 polymerisation

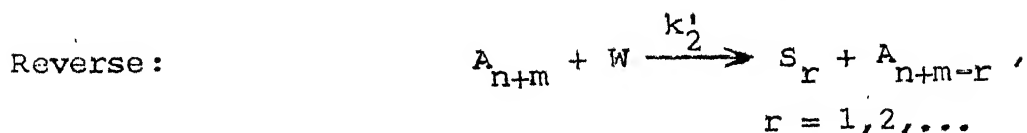
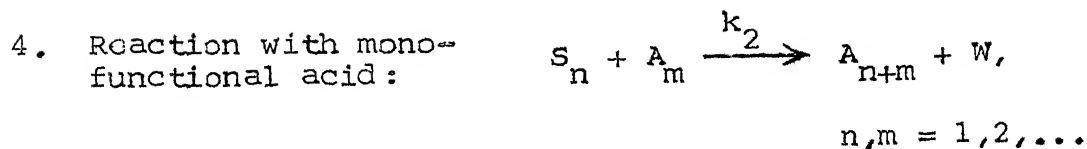
2. Polycondensation:



Note: The above rate constant will be k_2' if $(n+m)$ is even and for $r = \frac{1}{2}(n+m)$

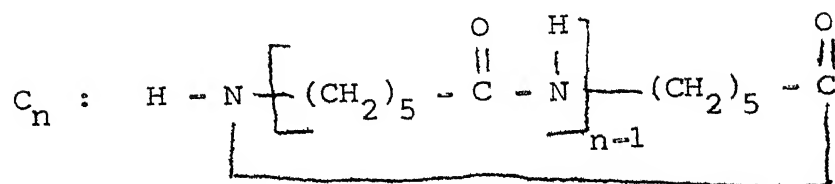
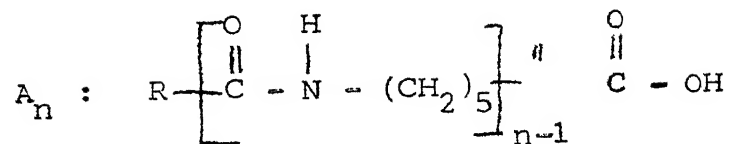
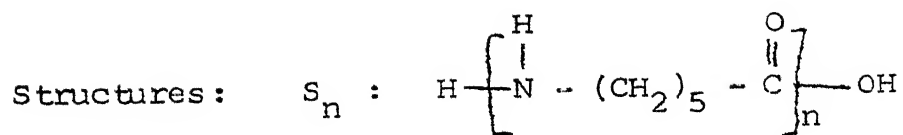


Note: The above two reactions are also valid between A-species and C-species



Contd...

Table B-1 (continued)



C_1 is the monomer..

Table B-2Rate equations in isothermal nylon 6 reactor

(for brevity, concentration terms are not enclosed by square brackets)

$$\frac{ds_1}{dt} = k_1 C_1 W - k_1' s_1 - 2k_2 s_1 \sum_{n=1}^{\infty} s_n + 2k_2' W \sum_{n=2}^{\infty} s_n - k_3 s_1 \sum_{n=1}^{\infty} n C_n \\ + \sum_{n=1}^{\infty} k_3' (n) s_{n+1} - k_2 s_1 \sum_{n=1}^{\infty} A_n + k_2' W \sum_{n=2}^{\infty} A_n$$

$$\frac{ds_n}{dt} = - 2k_2 s_n \sum_{m=1}^{\infty} s_m + k_2 \sum_{m=1}^{n-1} s_m s_{n-m} - k_2' W (n-1) s_n \\ + 2k_2' W \sum_{m=n+1}^{\infty} s_m - k_3 s_n \sum_{m=1}^{\infty} m C_m + k_3 \sum_{m=1}^{n-1} (n-m) s_m C_{n-m} \\ - s_n \sum_{m=1}^{n-1} k_3' (m) + \sum_{m=1}^{\infty} k_3' (m) s_{n+m} - k_2 s_n \sum_{m=1}^{\infty} A_m \\ + k_2' W \sum_{m=n+1}^{\infty} A_m, \quad n = 2, 3, 4$$

$$\frac{dc_1}{dt} = - k_1 C_1 W + k_1' s_1 - k_3 C_1 \sum_{n=1}^{\infty} s_n + k_3' (1) \sum_{n=2}^{\infty} s_n - k_3 C_1 \sum_{n=1}^{\infty} A_n \\ + k_3' (1) \sum_{n=2}^{\infty} A_n$$

$$\frac{dc_n}{dt} = - k_3 n C_n \sum_{m=1}^{\infty} s_m + k_3' (n) \sum_{m=n+1}^{\infty} s_m - k_3 n C_n \sum_{m=1}^{\infty} A_m \\ + k_3' (n) \sum_{m=n+1}^{\infty} A_m$$

Contd....

Table B-2 (continued)

$$\frac{dA_1}{dt} = -k_2 A_1 \sum_{n=1}^{\infty} S_n + k_2' W \sum_{n=2}^{\infty} A_n - k_3 A_1 \sum_{m=1}^{\infty} m C_m + \sum_{m=1}^{\infty} k_3' (m) A_{n+m}$$

$$\frac{dA_n}{dt} = -k_2 A_n \sum_{m=1}^{\infty} S_m + k_2 \sum_{m=1}^{n-1} A_m S_{n-m} - k_2' W (n-1) A_n + k_2' W \sum_{m=n+1}^{\infty} A_m$$

$$- k_3 A_n \sum_{m=1}^{\infty} m C_m + k_3 \sum_{m=1}^{\infty} (n-m) S_m C_{n-m} - A_n \sum_{m=1}^{\infty} k_3' (m)$$

$$+ \sum_{m=1}^{\infty} k_3' (m) A_{n+m}$$

Table B-3

Moment rate equations for nylon 6 polymerization

$$\frac{d\lambda_0}{dt} = k_1 MW - k_1' S_1 - k_2 \lambda_0^2 + k_2' W (\lambda_1 - \lambda_0) - k_2 \lambda_0 (\beta_0 + \beta_1 - \beta_0)$$

$$\frac{d\lambda_1}{dt} = k_1 MW - k_1' S_1 + k_3 \lambda_0 \gamma_2 - k_3 \left(\frac{1}{K_3} - B \right) (\lambda_0 - S_1) - k_3 B (\lambda_1 - \lambda_0) - k_2 \lambda_1 \beta_0 + \frac{k_2' W}{2} (\beta_2 - \beta_1)$$

$$\begin{aligned} \frac{d\lambda_k}{dt} = & k_1 MW - k_1' S_1 - 2k_2 \lambda_0 \lambda_k + k_2 \sum_{n=0}^k \frac{k!}{n!(k-n)!} \lambda_n \lambda_{k-n} \\ & - k_2' W (\lambda_{k+1} - \lambda_k) + 2k_2' W \sum_{m=2}^{\infty} \left\{ 1^k + 2^k + \dots + (m-1)^k \right\} S_m \\ & - k_3 \lambda_k \gamma_1 + k_3 \sum_{l=0}^k \frac{k!}{l!(k-l)!} \lambda_{k-l} \gamma_{l+1} \\ & - k_3 \left(\frac{1}{K_3} - B \right) \sum_{m=2}^{\infty} \left\{ (km)^{k-1} - \frac{k(k-1)}{2} m^{k-2} + \dots + (-1)^{k-1} \right\} S_m \\ & - k_3 B \sum_{n=1}^{\infty} \sum_{m=n+1}^{\infty} \left\{ (km)^{k-1} - \frac{k(k-1)}{2} m^{k-2} n + \dots + (-n)^{k-1} \right\} S_m \\ & - k_2 \lambda_k (\beta_0 + \beta_1) + k_2' W \sum_{m=2}^{\infty} \left\{ 1^k + 2^k + \dots + (m-1)^k \right\} \lambda_m \end{aligned}$$

$$\begin{aligned} \frac{d\gamma_k}{dt} = & -k_1 MW + k_1' S_1 - k_3 \lambda_0 \gamma_{k+1} + k_3 \left(\frac{1}{K_3} - B \right) (\lambda_0 - S_1) \\ & + k_3 B \sum_{n=1}^{\infty} \sum_{m=n+1}^{\infty} \left\{ 1^{k-1} + 2^{k-1} + \dots + (m-1)^{k-1} \right\} S_m \end{aligned}$$

Contd....

$$- k_3 \beta_0 \gamma_{k+1} + k_3 \left(\frac{1}{K_3} - B \right) (\beta_0 - A_1) + k_3 B \sum_{n=1}^{\infty} \sum_{m=n+1}^{\infty} \\ \left\{ 1 + 2^{k+1} + \dots + (m-1)^{k-1} \right\} A_m$$

$$\frac{d\beta_0}{dt} = -k_2 \beta_0 \lambda_0 + k_2 \beta_0 \lambda_0 - k_2' W (\beta_1 - \beta_0) + k_2' W (\beta_1 - \beta_0) \\ - k_3 \beta_0 \gamma_1 + k_3 \beta_0 \gamma_1 = 0$$

$$\frac{d\beta_k}{dt} = -k_2 \beta_k \lambda_0 + k_2 \sum_{m=0}^k \frac{k!}{m! (k-m)!} \beta_m \lambda_{k-m} - k_2' W (\beta_{k+1} - \beta_k) \\ + k_2' W \sum_{m=2}^{\infty} \left\{ 1^k + 2^k + \dots + (m-1)^k \right\} A_m - k_3 \beta_k \gamma_1 \\ + k_3 \sum_{l=0}^k \frac{k!}{l! (k-l)!} \beta_{k-l} \gamma_{l+1} - k_3 \left(\frac{1}{K_3} - B \right) \sum_{m=2}^{\infty} (km^{k-1} \\ - \frac{k(k-1)}{2} m^{k-2} + \dots + (-1)^{k-1}) A_m - k_3 B \sum_{n=1}^{\infty} \sum_{m=n+1}^{\infty} (km^{k-1} \\ - \frac{k(k-1)}{2} m^{k-2} n + \dots + (-n)^{k-1}) A_m$$

CHAPTER B-4

Computational Procedure

We have seen in the last chapter that the solution for the Nth moment requires the knowledge of the (N+1)th moment. Our next task is to (i) find the (N+1)th moment from the lower moments and (ii) to interpret the N moments in order to get the actual molecular weight distribution. We will adopt Min's approach⁽⁶⁰⁾ as has been done before by Krishnan⁽¹²⁾ and Gupta and Gandhi⁽⁶¹⁾.

The starting point in this method is the consideration that any continuous normalized distribution $G(x)$ can be expressed by the sum of an infinite number of Laguerre polynomials as follows:

$$G(x) = \frac{x^\alpha e^{-x}}{\Gamma(\alpha+1)} \sum_{n=0}^{\infty} C_n^\alpha L_n^\alpha(x) \quad (1)$$

where $L_n^\alpha(x)$ is the generalised Laguerre polynomial expressed as

$$L_n^\alpha(x) = \sum_{j=0}^n (-1)^j \frac{(n+\alpha+1)!}{(n-j)! (j+\alpha+1)!} \frac{x^j}{j!} \quad (2)$$

and α is a constant parameter.

The reason for using Laguerre polynomials is its more general orthogonal properties and the capacity of taking care of fractional moments as suggested by Min⁽⁶⁰⁾. Though theoretically an infinite number of polynomials are necessary for all practical purposes, it is possible to express $G(x)$ by a reasonably small number of polynomials. Here we have taken the upper limit of summation to be $N_{\max} = 9$. The actual choice of N_{\max} depends on the storage capacity of the computer, the accuracy

desired and the computation speed wanted. Once a finite number is used, because of the orthogonal properties, the unknown coefficients C_n^α , $n = 0$ to N_{\max} , can be computed if the first N_{\max} moments of the normalized distribution $G(x)$ are available

$$C_n^\alpha = \frac{\Gamma(\alpha+1) n!}{\Gamma(n+\alpha+1)} \sum_{j=0}^n (-1)^j \frac{\Gamma(n+\alpha+1)}{\Gamma(j+\alpha+1)(n-j)!} \frac{G_j}{j!} \quad (3)$$

Thus if the first N_{\max} moments of $G(x)$ are known,

C_n^α 's can be calculated therefrom and the actual distribution, $G(x)$, can be expressed with reasonable accuracy. Once this is done, the $(N_{\max} + 1)$ th and higher moments of the normalized distribution can be obtained using the general expression

$$G_k = \frac{\Gamma(\alpha+k+1)}{\Gamma(\alpha+1)} + \frac{1}{\Gamma(\alpha+1)} \sum_{n=1}^{N_{\max}} C_n^\alpha \sum_{j=0}^n (-1)^j \frac{\Gamma(n+\alpha+1) \Gamma(k+j+\alpha+1)}{(n-j)! j! \Gamma(j+\alpha+1)} \quad (4)$$

for derivation of (3) and (4) see Appendix (B.3)

The basic approach is thus to convert a given set of say 'k' original, unnormalized moments to a set of 'k' normalized moments. Next by the method described above, the higher normalized moments are obtained, from which is regenerated the $(k+1)$ th moment of the original distribution.

To convert the original moments to a set of normalized moments, the first task is to simulate the actual discrete distribution by a continuous distribution. Let us designate such a distribution by $M(v)dv$, which has to be converted to normalized distribution $G(x) dx$. Obviously it follows that

$$M(v) dv = \bar{M}_v^{(0)} G(x) dx \quad (5)$$

since $\int_0^{\infty} G(x) dx$ is unity.

Min has suggested that there be a linear relation between v and x e.g.,

$$v = a \cdot x. \quad (6)$$

the constant 'a' has to be determined from other conditions.

Since ' α ' is a free parameter in eq.(3), it is usually customary to put C_1^α as zero. In such a case it follows from eq.(3) that

$$G_1 = 1 + \alpha \quad (7)$$

Now from eq.(5) we can write

$$\int_0^{\infty} v^k M(v) dv = \bar{M}_v^{(0)} \cdot \int_0^{\infty} v^k G(x) dx \text{ for any value of 'k'}$$

or

$$\bar{M}_v^{(k)} = \bar{M}_v^{(0)} a^k \bar{G}_x^{(k)} \quad (8)$$

Putting $k = 1$ in eq. (8), we get

$$a = \frac{\bar{M}_v^{(1)}}{(1+\alpha) \bar{M}_v^{(0)}} \quad v = \frac{\bar{M}_v^{(1)}}{(1+\alpha) \bar{M}_v^{(0)}} x \quad (9)$$

and

$$\bar{M}_v^{(k)} = \bar{M}_v^{(0)} \left[\frac{\bar{M}_v^{(1)}}{(1+\alpha) \bar{M}_v^{(0)}} \right]^k \bar{G}_x^{(k)} \quad (10)$$

Eqn.(10) relates the original moments to the normalized moments. It should be noted that this eqn. works only for $k=2$ and above. For $k=1$ eqn.(10) simply becomes eq.(7). It only shows that ' α ' and G_1 are inter-related but neither has a unique value. To fix a unique value of ' α ', Min has suggested that C_2^α be also put to zero. For such a case, eqn.(3) yields

$$G_2 = (1+\alpha) (2 + \alpha) = G_1 (1 + G_1) \quad (11)$$

On the other hand putting $k = 2$ in eq.(10) yields

$$\frac{\bar{M}_v^{(2)} \bar{M}_v^{(0)}}{\bar{M}_v^{(1)2}} = \frac{G_2}{G_1^2} \quad (12)$$

Combining eqs. (11) and (12) one gets

$$G_1 = \frac{1}{\frac{\bar{M}_v^{(2)} \bar{M}_v^{(0)}}{\bar{M}_v^{(1)2}} - 1} \quad (13)$$

Thus G_1 and hence α get uniquely determined.

Once the $G(x)$ distribution is obtained, $M(v)$ distribution can also be obtained by making use of equations (5) and (9); yielding

$$M(v) = \frac{\bar{M}_v^{(0)}(1+\alpha)}{\bar{M}_v^{(1)}} G(x) \quad \left| \quad x = \frac{\bar{M}_v^{(0)}(1+\alpha)}{\bar{M}_v^{(1)}} \cdot v \right. \quad (14)$$

Thus for integral values of v , $M(v)$ can be calculated; and though, strictly speaking, $M(v)$ is a density distribution function and not the actual distribution, i.e. actual discrete distribution of say S_n is related as $\sum_{n=a}^{b\Delta} S_n = \int_a^{b\Delta} M(v) dv$; to calculate individual concentration S_n , the evaluation of $M(v)$ at that value of v is sufficient. Because $\Delta v = 1$ in the integral, and $M(v)$ can be taken to be equal to S_n . The same remarks apply to all other distributions.

CHAPTER B-5

Computational Problems and Discussions

There are two main computational problems present in this case. Firstly, it was seen that though the value of α suggested by Min gives faster computation, it does not necessarily give good convergence. The convergence can be best tested in the following way. While using Min's procedure we start initially from a set of N_{\max} number of unnormalized moments from which G_k 's are calculated. Now we may recalculate the normalized moments by putting $k = 2, 3, \dots, N_{\max}$ in Eq.(4) in Chapter B-4, which, when unnormalized, can be compared to the original set. The sum of the deviations from the original moments constitutes the best convergence criterion. The same has been suggested by Sicotte⁽⁶³⁾ also. For a particular set of original moments, this sum of deviation is a function of α only, and it was seen that in most of the cases, the α suggested by Min gives a poor convergence. The value of α that gives the best convergence may be obtained by an optimization process, where the sum of deviation is to be minimized. This α is subsequently used to compute the $(N_{\max}+1)$ th moment.

The second problem comes while applying Min's method to the ring length distribution. It should be noted that there is no way to directly find the zeroth ring moment, since it necessitates the summing of a harmonic progression, for

which there is no convenient formula. But the value of zeroth moment is essential in order to apply Min's method. Hence one has to think of some way to circumvent these problems.

In the present case we have used α as a truly free parameter for the chain distribution and obtained α by an optimization as justified above. One surprising finding is that integer values of α always give better convergence. This practically makes it an integer optimization process. However, it is felt that more studies are warranted in this direction.

In case of rings, α has again been used as a free parameter. G_1 is obtained from Eq.(7) and the zeroth moment calculated from G_1 by Eq.(13), followed by the optimization process same as in case of chains. The difference in the procedures for chains and rings is that in the former G_1 is calculated from the zeroth moment and in the latter, it is just the opposite way. This is possible presumably because there are two inherent degrees of freedom in this computational scheme.

Using the approach outlined above we have tried to solve the thirty coupled differential equations which arise in the reaction simulation viz. the rate equations for the zeroth and first nine moments of both the chains species and rate equation for monomer and the rate equations for the first to ninth ring moments using a four-point Runge-Kutta-Gill method⁽⁶⁶⁾ with an initial time increment of 0.1 hour. The

rate and equilibrium constants of Reinschuessel⁽¹⁾ are used for an initial water concentration of 0.44 mole/kg and temperature 235°C.

The molecular weight distribution for the chains can be found by the method outlined in chapter four and they match within some errors with the data given by Gupta et al.⁽⁶⁴⁾. The same method to find the ring length distribution for the macrocyclics was not very successful, however, particularly at the low values of the polymerisation time. This is presumably because the monomer concentration is so much more than the total concentration of macrocyclics that the distribution is not very well defined (it should be noted that in the calculation of ring moments the monomer concentration is also included). This problem may be circumvented by a proper scaling procedure in which the monomer concentration is deducted from each of the ring moments. This, understandably, won't instill any significant error because the contribution by the monomer concentration is the same to all of the ring moments. By this scaling process a reasonable distribution may be obtained for which the concentration for $n=1$ should be ideally zero. In fact, minimization of the concentration of $n=1$ after scaling in itself may be selecting criteria for α , but in this case the least squared deviation may be poor. It should be admitted that we are yet to establish a really sound selection criterion.

But the most difficult problem which could not be overcome in the present case and which was the cause of the failure, was the stability problem. That is to say, the values of dY_k/dt for larger values of k become so highly negative after about two hours of polymerization, that Y_k 's themselves gradually become negative and the computation becomes unstable. This instability is typical of nylon-6 polymerization as has been reported earlier by Gupta et al.⁽⁶⁷⁾. In their case they used individual species equations and commented that the problem may be overcome by sufficiently decreasing Δt . But in our case we could not get over the problem even with a value of $\Delta t = 0.001$ hr. This also put into doubt the acceptability of the method in which we are computing the zeroth ring moment. This may well be one of the reasons for this instability. The zeroth moment can be evaluated, for example by curve fitting the harmonic progression by some suitable polynomial. But whatever may be the reason, unless we are able to solve this problem on a sound theoretical basis, it is not thought worthwhile to go on decreasing Δt to solve the instability problem.

In conclusion it will be said that here our aim was mainly to establish a generalized technique so that the simulation can be done for any set of operating and system variables. For this particular case, we have not been successful due to problems outlined above, but it is hoped that, with more in-depth study, these problems can be solved. This method can be subsequently used for better reactor designs and optimization.

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Appendix A-1

Definition

$$S_{n-1,k} = 1+2^k + 3^k + \dots + (n-1)^k$$

$$S_{n-1,1} = \frac{n(n-1)}{2}$$

$$S_{n-1,2} = \frac{2n^3-3n^2+n}{6}$$

$$S_{n-1,3} = \frac{n^4-2n^3+n^2}{4}$$

$$S_{n-1,4} = \frac{6n^5-15n^4+10n^2-n}{30}$$

$$S_{n-1,5} = \frac{2n^6-6n^5+5n^4-n^2}{12}$$

$$S_{n-1,6} = \frac{12n^7-42n^6+42n^5-14n^3+2n}{84}$$

$$S_{n-1,7} = \frac{3n^8-12n^7+14n^6-7n^4+2n^2}{24}$$

$$S_{n-1,8} = \frac{10n^9-45n^8+60n^7-42n^5+20n^3-3n}{90}$$

$$S_{n-1,9} = \frac{2n^{10}-10n^9+15n^8-14n^6+10n^4-3n^2}{20}$$

Sample rate equations for the moments

Bifunctional chain moments : $\frac{d\lambda_8}{dt} = k_1 MW - k_1^i s_1 + k_2(16\lambda_1\lambda_7 + 56\lambda_2\lambda_6$
 $+ 112\lambda_3\lambda_5 + 70\lambda_4^2) - k_2^i W (\lambda_9 - \lambda_8)$
 $+ 2k_2^i W (\frac{10\lambda_9 + 45\lambda_8 + 60\lambda_7 - 42\lambda_5 + 20\lambda_3 - 3\lambda_1}{90})$
 $+ k_2(8\lambda_7\gamma_2 + 28\lambda_6\gamma_3 + 56\lambda_5\gamma_4 + 70\lambda_4\gamma_5 + 56\lambda_3\gamma_6$
 $+ 28\lambda_2\gamma_7 + 8\lambda_1\gamma_8 + \lambda_0\gamma_9)$
 $- k_3(\frac{1}{k_3} - B)(8\lambda_7 - 28\lambda_6 + 56\lambda_5 - 70\lambda_4 + 56\lambda_3$
 $- 28\lambda_2 + 8\lambda_1 - \lambda_0 - s_1)$
 $- k_3 B - 6(\lambda_8 - \lambda_7) + 56(\frac{2\lambda_8 - 3\lambda_7 + \lambda_6}{6}) - 70$
 $(\frac{\lambda_8 - 2\lambda_7 + \lambda_6}{4}) + 56(\frac{6\lambda_8 - 15\lambda_7 + 10\lambda_6 - \lambda_4}{30})$
 $- 28(\frac{2\lambda_8 - 6\lambda_7 + 5\lambda_6 - \lambda_4}{12}) + 8(\frac{12\lambda_8 - 42\lambda_7 + 42\lambda_6 - 14\lambda_4 + 2\lambda_2}{84}$
 $- (\frac{3\lambda_8 - 12\lambda_7 + 40\lambda_6 - 7\lambda_4 + 2\lambda_2}{24})$
 $- k_2\lambda_8\beta_0 + k_2^i W(\frac{10\beta_9 - 45\beta_8 + 60\beta_7 - 42\beta_5 + 20\beta_3 - 3\beta_1}{90})$

Monofunction Chain Moments : $\frac{d\beta_8}{dt} = k_2(\beta_0\lambda_8 + 8\beta_1\lambda_7 + 28\beta_2\lambda_6 + 56\beta_3\lambda_5 + 70\beta_4\lambda_4$
 $+ 56\beta_5\lambda_3 + 28\beta_6\lambda_2 + 8\beta_7\lambda_1) - k_2^i W(\beta_9 - \beta_8)$
 $+ k_2^i W(\frac{10\beta_9 - 45\beta_8 + 60\beta_7 - 42\beta_5 + 20\beta_3 - 3\beta_1}{90}) + k_3$
 $(8\beta_7\gamma_2 + 28\beta_6\gamma_3 + 56\beta_5\gamma_4 + 70\beta_4\gamma_5 + 56\beta_3\gamma_6 + 28\beta_2\gamma_7$
 $+ 8\beta_1\gamma_8 + \beta_0\gamma_9) - k_3(\frac{1}{k_3} - B)(8\beta_7 - 28\beta_6 + 56\beta_5 - 70\beta_4$
 $+ 56\beta_3 - 28\beta_2 + 8\beta_1 - \beta_0 - A_1)$

$$\begin{aligned}
 & -k_3 B \left[-6(\beta_6 - \beta_7) + 56 \left(\frac{2\beta_8 - 2\beta_7}{6} \right) - 70 \right. \\
 & \left. \left(\frac{\beta_8 - 12\beta_7 + \beta_6}{30} \right) + 56 \left(\frac{6\beta_8 - 15\beta_7 + 10\beta_6 - \beta_4}{30} \right) \right. \\
 & - 28 \left(\frac{2\beta_8 - 6\beta_7 + 5\beta_6 - \beta_4}{12} \right) + 8 \left(\frac{12\beta_6 - 12\beta_7 + 12\beta_6 - 1\beta_4}{8} \right) \\
 & \left. \left(\frac{+2\beta_2}{24} \right) - \left(\frac{3\beta_8 - 12\beta_7 + 14\beta_6 - 7\beta_4 + 2\beta_2}{24} \right) \right]
 \end{aligned}$$

Ring Moments:

$$\begin{aligned}
 \frac{d\gamma_8}{dt} &= -k_1 MW + k_1 S_1 - k_3 \lambda_0 \gamma_9 + k_3 \left(\frac{1}{K_3} - B \right) (\lambda_0 - S_1) \\
 &+ k_3 B \left(\frac{3\lambda_8 - 12\lambda_7 + 14\lambda_6 - 7\lambda_4 + 2\lambda_2}{24} \right)
 \end{aligned}$$

$$\begin{aligned}
 & -k_3 \beta_0 \gamma_9 + k_3 \left(\frac{1}{K_3} - B \right) (\beta_0 - A_1) + k_3 B \\
 & \left(\frac{3\beta_8 - 12\beta_7 + 14\beta_6 - 7\beta_4 + 2\beta_2}{24} \right)
 \end{aligned}$$

APPENDIX B-3

MIN'S METHOD

$$G(x) = \frac{x^\alpha e^{-x}}{\Gamma(\alpha+1)} \sum_{n=0}^{N_{\max}} L_n^\alpha(x) C_n^\alpha$$

where $L_n^\alpha(x) = \sum_{j=0}^n (-1)^j \frac{\Gamma(n+\alpha+1)}{(n-j)! \Gamma(j+\alpha+1)} \frac{x^j}{j!}$

Now, $G(x) L_n^\alpha(x) = \frac{x^\alpha e^{-x}}{\Gamma(\alpha+1)} L_n^\alpha(x) \sum_{m=0}^{N_{\max}} C_m^\alpha L_m^\alpha(x)$

Or

$$\sum_{j=0}^n (-1)^j \binom{n+\alpha}{n-j} \frac{x^j}{j!} G(x) = \frac{x^\alpha e^{-x}}{\Gamma(\alpha+1)} L_n^\alpha(x) \sum_{m=0}^{N_{\max}} C_m^\alpha L_m^\alpha(x)$$

Integrate

$$\int_{x=0}^{\infty} \sum_{j=0}^n (-1)^j \binom{n+\alpha}{n-j} \frac{x^j}{j!} G(x) dx = \frac{\Gamma(n+\alpha+1)}{\Gamma(\alpha+1) n!} C_n^\alpha$$

$$C_n^\alpha = \frac{\Gamma(\alpha+1)n!}{\Gamma(n+\alpha+1)} \sum_{j=0}^n (-1)^j \binom{n+\alpha}{n-j} \frac{\bar{G}_x^{(j)}}{j!}$$

Now $\bar{G}_x^{(k)} = \int_0^\infty x^k G(x) dx =$

$$= \int_0^\infty \sum_{n=0}^{N_{\max}} C_n^\alpha \frac{x^{k+\alpha} e^{-x}}{\Gamma(\alpha+1)} \left(\sum_{j=0}^n (-1)^j \binom{n+\alpha}{n-j} \frac{x^j}{j!} \right) dx$$

or rearranging,

$$\bar{G}_x^{(k)} = \sum_{n=0}^{N_{\max}} \frac{C_n^\alpha}{\Gamma(\alpha+1)} \left\{ \sum_{j=0}^n (-1)^j \frac{(n+\alpha)!}{(j+\alpha)!} \frac{(k+j+\alpha)!}{j! (n-j)!} \right\}$$
